DISARM PROJECT

Policy informing document: Final research results

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EXECUTIVE SUMMARY

Marine dump sites of conventional and chemical munitions occur in numerous locations in our seas and ocean. They pose potential risks for the marine environment and human health and present us with complex challenges in terms of monitoring and management. A well-known example is the Paardenmarkt dump site, near the coast of Knokke-Heist (Belgium), where a presumed 35,000 tonnes of WW1 chemical and conventional munition are buried just a few meters under the seafloor. Until now, the government has adopted a management approach to leave the site undisturbed and monitor the state of the Paardenmarkt on a regular basis. Yet, it is deemed increasingly important to address some important knowledge gaps about the dump site to unlock alternative management options and assess potential (future) environmental or societal hazards. These knowledge gaps span different disciplines and are often interlinked: e.g. How much munition is exactly present? What is the state of the munition? What is the exact burial depth and distribution of the munition? How is the contamination evolving within the sediment and in the overlaying water column? As such, the DISARM project has adopted an integrated scientific approach to address some of the unanswered research questions and provide the necessary underpinning for the risk assessment and management of the Paardenmarkt munition dump site. It should be noted that many project results can be transposed to other marine chemical munition dump sites worldwide.

Characterising the subsurface of the Paardenmarkt dump site

In first instance, DISARM has achieved significant progress in the further characterisation of the subsurface of the Paardenmarkt. As it is one of the major challenges to map the 3D distribution of the munition in the sediment, an innovative approach was tested, using high-resolution multi-sensor magnetometry, both at sea and on land, complemented by advanced inverse modelling. This approach proved capable of detecting objects and small clusters of objects, thereby distinguishing individual clusters in areas previously identified as large single clusters. Additionally, it provided a better understanding of the depth and mass of the objects and clusters. Within the DISARM project, this methodology has been tested in a well-defined subarea of the dump site. After further refining, the developed approach can be applied on the entire Paardenmarkt dump site and will greatly improve the knowledge about the distribution and mass of the buried munition. In addition, the DISARM project prepared to conduct a unique and precise sounding and sampling campaign within the sediment close to the munition but was not able to proceed with this action within the lead time of the project. However, it was established that the technology and know-how are (largely) in place to carry out this type of operation in the (near) future. Moreover, great progress was made concerning the technical boundary conditions and the legal aspects on liability insurance of such campaigns.

Furthermore, a thorough characterisation of the biogenic gas content and the groundwater flow in the region was conducted for the very first time. Most importantly, the mapping of the freshwater submarine groundwater discharge ruled out any risk of contamination from the Paardenmarkt dump site towards land-based freshwater lenses in the coastal zone. The very high concentrations of methane and carbon dioxide observed in the sediments do not impose any direct risk but - on the contrary - are expected to slow down the corrosion rate and may stimulate biodegradation of toxic compounds.

State of the munition and explosion risk

The DISARM project has greatly invested in establishing a model to predict long-term corrosion processes on munition shells in marine sediments, based on the outcomes of mesocosm and lab studies. This research has demonstrated that the prevailing corrosion rates of zamak, messing and iron are quite slow compared to other regions in the world. Moreover, the corrosion research confirms that the current situation on the Paardenmarkt, where the munition is buried underneath a few meters of sediment in an anaerobic environment, creates very low corrosion rates which likely slows down the leakage

of harmful munition-related compounds. It is crucial to note that a potential re-exposure of the munition shells to oxygen (for example by bringing them to the surface), is expected to significantly accelerate the corrosion process.

A detailed study of 100-year-old explosives indicates that their explosive properties are retained and that their sensitivity has not changed. Yet, because the munition is buried beneath a few meters of sediment, the aerial shock wave resulting from an accidental explosion of (part of) the munition at the Paardenmarkt will be significantly attenuated. Moreover, the fact that the munition is most likely not armed or equipped with an arming system, further reduces the risk. Taking into account that the risk of an accidental explosion is already extremely low, the conducted explosion risk analysis concluded that, at present, there is virtually no risk of harm to humans resulting from a potential explosion of the munition buried at the Paardenmarkt site (except for persons present at the dump site).

From an integrated chemical assessment of the Paardenmarkt towards an early warning capacity

The DISARM research has achieved notable methodological advancements, enabling the detection of toxic substances at extremely low concentrations in sediment and water. As a result, (very) low concentrations of munition-related compounds were detected at multiple locations at the Paardenmarkt. These new developments pave the way towards an early warning system for the site that enables timely action in case an enhanced leakage of toxic compounds would occur.

Given the risk of leakage of toxic compounds from the buried munition, an important part of the DISARM project focused on progressing our knowledge about the (eco)toxicological effects of various munition-related chemicals on bacteria, copepods, algae and fish. Adhering to European ECHA guidelines, an environmental risk assessment was conducted using the gathered ecotoxicity data. Widespread leakage of toxic compounds was detected at the Paardenmarkt dump site (in 85% of the sediment samples and 91% of the bottom water samples over the period of 2021-2023). At the majority of the sampling locations, the risk was negligible, however, the measured concentrations of mixtures of toxic compounds at a few locations are cause for concern (2%) or pose a risk for bottom-dwelling organisms (0.5%). Targeted sampling on locations where clusters of munitions could be expected based on earlier leakage detection (2019) or magnetic measurements (2023) further increased the share of samples where a cause of concern (15%) or risk (2%) for epibenthic organisms was observed. It is highlighted that future research is needed with respect to the effects of mixtures of toxic compounds and bioaccumulation/ biomagnification effects.

Once in the water column, the contaminants are diffused and dispersed by the currents and are subject to additional degradation. This spatiotemporal fate of the pollutants has been estimated and mapped using the integrated (hydro-sediment-chemical) transport model COHERENS for different concentration scenarios. However, it should be noted that these findings are based on concentrations coming from only a limited number of locations on the Paardenmarkt, while typically the contamination measurements are highly spatially variable.

Developing bioremediation as an innovative new management option

The DISARM project managed to demonstrate the ability of indigenous microorganisms to effectively degrade toxic compounds deriving from TNT and Clark metabolites in a marine environment. Also, the biodegradation of toxic mustard gas (Yperite) compounds was observed for the first time. However, it is important that, subsequently to this pioneering work, more knowledge is gathered on how the different microbial communities interact with each other and the functional role each of them plays in such ecosystems. These insights will in turn prove highly valuable in validating the role of microorganisms as effective, low-risk bioremediation agents in (marine) munition dump sites. Moreover, these findings will offer enhanced guidance on various in-situ strategies, delineating between options such as passive monitoring of the prevailing processes or actively stimulating biodegradation.

Recommendations for policy

- It is recommended to **expand the novel gradiometric technique, combined with inverse modelling**, to the entire Paardenmarkt dump site. This will not only enhance our understanding of the 3D distribution and mass of the munition but will also improve future sampling strategies (provided a very precise positioning);

- As widespread leakage of toxic compounds was observed at the Paardenmarkt dump site and the risk assessment pointed at location-specific concerns and risks, the **current monitoring effort should be further expanded towards a fully operational early warning system.** This should include both observing and modelling components, accounting for the sediment, pore water and overlaying water column, to allow timely action in case of increased leakage of these compounds. Moreover, it is recommended to invest in effect assessments of mixtures of toxic substances (including bioaccumulation/biomagnification and potenial effects on human health) and promising novel monitoring techniques such as eDNA for biodiversity monitoring and biomonitoring based on microbial communities;

- It is advised to **make further progress with a sampling campaign in the upper meters of the sediment** of the Paardenmarkt. It was demonstrated that the technology and know-how is (largely) in place to conduct such a campaign in a safe way. This would mean a major advance in our understanding of the contamination within the sediment and state of the munition. Moreover, this would greatly reduce the prevailing uncertainties of (potential) alternative management scenarios for the site;

- DISARM has aggregated and archived both new and existing data and information in an integrated geoportal. It is highly recommended to **further invest in this data system to adequately archive and integrate the data and results** of future sampling and observation campaigns;

- Overall, the results of DISARM concur with the management approach that has been adopted until now to leave the Paardenmarkt undisturbed and monitor its state. Yet, the detection of (very) low munition compound concentrations at various locations of the dump site, highlights the need to **accelerate the investment in closing some of the remaining critical knowledge gaps** (e.g. the leakage flux and volume, effects of mixtures of toxic compounds/chronic exposure, bioaccumulation/biomagnification effects, the potential of stimulation of biodegradation processes). This will allow to further assess and refine the prevailing risks of the dump site and define the required management option(s) for the future.

DISCLAIMER

The current policy-informing report is a final deliverable of the DISARM project, funded by the Research Foundation Flanders (FWO). The report fully builds on the conducted research and provides a concise overview of the scientific results obtained within the framework of the project, i.e. a comprehensive characterisation of the Paardenmarkt munition dump site. Even though the DISARM project adopted an integrated approach, pertinent knowledge gaps remain (e.g. security threats and potential effects on human health) that were not or only preliminary investigated in the project and as such, are not addressed in this document.

SAMENVATTING

Stortplaatsen van conventionele en chemische munitie bevinden zich op talloze locaties in onze zeeën en oceaan. Ze vormen potentiële risico's voor het mariene milieu en de menselijke gezondheid en stellen ons voor complexe uitdagingen op het gebied van monitoring en beheer. Een gekend voorbeeld is de Paardenmarkt munitiestortplaats, gelegen voor de kust van Knokke-Heist (België), waar naar schatting 35.000 ton chemische en conventionele munitie uit de Eerste Wereldoorlog begraven ligt op slechts enkele meters onder de zeebodem. Tot op heden heeft de overheid ervoor gekozen om een beheersaanpak te hanteren waarbij de munitiestortplaats onaangeroerd blijft en de toestand van de Paardenmarkt regelmatig wordt gemonitord. Desalniettemin is het aangewezen om enkele belangrijke kennislacunes met betrekking tot de stortplaats aan te pakken. Dit is essentieel om alternatieve beheeropties te kunnen verkennen en om mogelijke (toekomstige) milieu- of maatschappelijke risico's te beoordelen. Deze kennishiaten beslaan verschillende disciplines en zijn veelal met elkaar verbonden: bv. Hoeveel munitie is er exact aanwezig? Wat is de staat van de munitie? Wat is de exacte begraafdiepte en verspreiding van de munitie? Hoe evolueert de contaminatie in het sediment en in de waterkolom? Het DISARM-project past daarom een geïntegreerde wetenschappelijke benadering toe om diverse onbeantwoorde onderzoeksvragen aan te pakken en de vereiste kennisbasis te bieden voor de risicobeoordeling en het beheer van de Paardenmarkt munitiestortplaats. Het dient aangestipt te worden dat veel resultaten van het project daarbij relevant zijn voor andere mariene chemische munitiestortplaatsen over heel de wereld.

Karakterisering van de ondergrond van de Paardenmarkt

In de eerste plaats heeft DISARM aanzienlijke vooruitgang geboekt in de verdere karakterisering van de ondergrond van de Paardenmarkt munitiestortplaats. Gezien de grote uitdaging om de 3D-distributie van munitie in het sediment in kaart te brengen, werd een innovatieve aanpak getest. Deze aanpak hanteerde multi-sensor, hoge-resolutie magnetometrie, zowel op zee als op het land, aangevuld met geavanceerde inverse modellering. Deze methode bleek niet alleen in staat objecten en kleine clusters te detecteren, maar maakte het ook mogelijk om een onderscheid te maken tussen individuele clusters in gebieden die voorheen als grote afzonderlijke clusters werden geïdentificeerd. Daarnaast bood het de mogelijkheid om een beter inzicht te krijgen in zowel de diepte als de massa van zowel de individuele objecten als de clusters. Binnen het DISARM-project is deze methodologie toegepast in een specifiek deelgebied van de stortplaats. Na verdere verfijning kan de ontwikkelde aanpak worden uitgebreid naar de gehele Paardenmarkt stortplaats, wat zal resulteren in een verbeterde kennis over de verspreiding en hoeveelheid van de begraven munitie. Daarnaast nam het DISARM-project zich voor om een unieke en nauwkeurige sondeer- en bemonsteringscampagne uit te voeren in het sediment dicht bij de munitie. Deze actie kon evenwel niet worden uitgevoerd binnen de doorlooptijd van het project. Wel werd er aangetoond dat de technologie en knowhow (grotendeels) voorhanden zijn om dit soort operaties in de (nabije) toekomst uit te voeren. Bovendien werd aanzienlijke vooruitgang geboekt met betrekking tot de technische vereisten en juridische aspecten met betrekking tot aansprakelijkheid en verzekeringen voor dergelijke campagnes.

Bovendien werd voor het eerst een grondige karakterisering van het aanwezige biogene gas en de grondwaterstroming in de regio uitgevoerd. Belangrijk is dat de kartering van het grondwater in de zeebodem ter hoogte van de Paardenmarkt wijst op een ondergrondse zoetwaterafvoer in zeewaartse richting, waardoor zoetwaterlenzen in de kustzone (landzijde) gevrijwaard worden van enige potentiële verontreiniging afkomstig van de Paardenmarkt. De zeer hoge concentraties methaan en kooldioxide die in het sediment werden waargenomen vormen geen direct risico, maar zullen naar verwachting eerder de corrosiesnelheid vertragen en de biodegradatie van toxische verbindingen stimuleren.

Staat van de munitie en explosierisico

Het DISARM-project heeft aanzienlijke inspanningen geleverd om een model te ontwikkelen dat langetermijncorrosieprocessen van munitiehulzen in mariene sedimenten kan voorspellen. Het model is gebaseerd op de resultaten van mesokosmos- en laboratoriumstudies. Dit corrosieonderzoek heeft aangetoond dat de huidige corrosiesnelheden van zamak, messing en ijzer vrij laag zijn in vergelijking met andere regio's in de wereld. Bovendien

bevestigt het corrosieonderzoek dat de huidige situatie op de Paardenmarkt, waarbij de munitie begraven ligt onder enkele meters sediment in een anaerobe omgeving, resulteert in zeer lage corrosiesnelheden, wat waarschijnlijk de lekkage van schadelijke munitiecomponenten vertraagt. Er wordt verwacht dat het opnieuw blootstellen van de munitiehulzen aan zuurstof (bv. door ze naar de oppervlakte te brengen) het corrosieproces aanzienlijk zal versnellen.

Een gedetailleerde studie van 100 jaar oude explosieven geeft aan dat de explosieve eigenschappen behouden blijven en dat de explosiegevoeligheid niet is veranderd. Doordat de munitie evenwel begraven ligt onder enkele meters sediment, zal de schokgolf in de lucht als gevolg van een accidentele explosie van (een deel van) de munitie op de Paardenmarkt aanzienlijk worden gedempt. Gezien het reeds extreem lage risico op een dergelijke explosie, concludeert de explosierisicoanalyse dat er momenteel vrijwel geen risico is op menselijke slachtoffers als gevolg van een mogelijke explosie van de munitie die begraven ligt op de Paardenmarkt (met uitzondering van personen die zich op dat moment op de stortplaats bevinden).

Van een geïntegreerde chemische beoordeling van de Paardenmarkt naar een vroegtijdige waarschuwingscapaciteit

Het DISARM-onderzoek heeft significante methodologische vooruitgang geboekt op het vlak van de detectielimiet van toxische stoffen in sediment en water, waarbij tegenwoordig extreem lage concentraties kunnen worden gedetecteerd. Zo werden tijdens de looptijd van het project op tal van locaties (zeer) lage concentraties aan munitiegerelateerde verbindingen gedetecteerd. Deze nieuwe ontwikkelingen leggen de basis voor een vroegtijdig waarschuwingssysteem voor deze site, waarmee tijdig actie kan worden ondernomen in het geval een verhoogde lekkage van toxische stoffen wordt gedetecteerd.

Gezien het risico op lekkage van toxische stoffen uit de begraven munitie, richtte een aanzienlijk deel van het DISARM-project zich op het vergroten van de kennis over de (eco)toxicologische effecten van verschillende munitie-gerelateerde chemicaliën op bacteriën, copepoden, algen en vissen. In overeenstemming met de Europese ECHA-richtlijnen werd een milieurisicobeoordeling uitgevoerd op basis van de verzamelde ecotoxiciteitsgegevens. Een wijdverspreide lekkage van toxische stoffen werd gedetecteerd op de Paardenmarkt stortplaats (in 85% van de sedimentmonsters en 91% van de bodemwatermonsters tussen 2021 en 2023). Op het merendeel van de bemonsteringslocaties was het risico verwaarloosbaar, maar de gemeten concentraties van mengsels van toxische stoffen op enkele locaties zijn reden tot bezorgdheid (2%) of vormen een risico voor bodemorganismen (0.5%). Gerichte staalnames op locaties waar clusters van munitie konden worden verwacht op basis van eerdere lekkagegegevens (2019) of magnetische metingen (2023) verhoogden het aandeel monsters waar een reden tot bezorgdheid (15%) of risico (2%) voor epibentische organismen werd waargenomen.

Eenmaal in de waterkolom worden de contaminanten verspreid door stromingen en ondergaan ze een verdere afbraak. Dit spatiotemporele lot van de contaminanten werd voor verschillende concentratiescenario's berekend en in kaart gebracht met behulp van het geïntegreerde (hydro-sediment-chemische) transportmodel COHERENS. Hierbij moet worden opgemerkt dat deze bevindingen gebaseerd zijn op concentraties afkomstig van slechts een beperkt aantal locaties op de Paardenmarkt, terwijl contaminatiewaarden doorgaans worden gekenmerkt door een sterke ruimtelijke en temporele variatie.

Ontwikkeling van bioremediatie als innovatieve nieuwe beheersoptie

Het DISARM-project is erin geslaagd aan te tonen dat lokale micro-organismen in staat zijn om toxische verbindingen afkomstig van TNT en Clark-metabolieten effectief af te breken in een marien milieu. Ook werd voor het eerst de biologische afbraak van giftige mosterdgasverbindingen (Yperiet) waargenomen. Het is echter belangrijk dat er na dit baanbrekende werk meer kennis wordt verzameld over hoe de verschillende microbiële gemeenschappen met elkaar interageren en welke functionele rol elk van hen speelt in dergelijke ecosystemen. Deze inzichten zullen op hun beurt zeer waardevol blijken bij het valideren van de rol van micro-organismen als effectieve, laagdrempelige bioremedianten op (mariene) munitiestortplaatsen. Bovendien zullen deze bevindingen een betere leidraad bieden voor verschillende in-situ strategieën, waarbij een onderscheid wordt gemaakt tussen opties zoals passieve monitoring van de heersende processen of het actief stimuleren van biologische afbraak.

Beleidsaanbevelingen

- Het wordt aanbevolen om **de nieuwe magnetometrische techniek, gecombineerd met inverse modellering, uit te breiden** naar de gehele Paardenmarkt stortplaats. Dit zal niet alleen ons begrip van de 3D-distributie en massa van de munitie verbeteren, maar ook toekomstige bemonsteringsstrategieën optimaliseren (mits een zeer nauwkeurige positionering);
- Aangezien er op de Paardenmarkt stortplaats wijdverspreide lekkage van giftige stoffen werd waargenomen en de risicobeoordeling wees op locatiespecifieke bezorgdheden en risico's, **wordt aanbevolen de huidige monitoringsinspanningen verder uit te breiden tot een volledig operationeel vroegtijdig waarschuwingssysteem.** Dit zou zowel observatie- als modelcomponenten moeten omvatten, rekening houdend met het sediment, poriënwater en de bovenliggende waterkolom, zodat tijdig actie kan worden ondernomen in geval van verhoogde lekkage van schadelijke stoffen. Daarnaast wordt het aanbevolen te investeren in effectbeoordelingen van mengsels van toxische stoffen, inclusief bioaccumulatie/biomagnificatie en potentiële effecten op de menselijke gezondheid. Verder moet ook het potentieel van nieuwe veelbelovende monitoringtechnieken, zoals eDNA voor biodiversiteitsmonitoring en biomonitoring op basis van microbiële gemeenschappen, nagegaan worden;
- Er wordt geadviseerd om **verdere vooruitgang te boeken met een bemonsteringscampagne van het diepere sediment** van de Paardenmarkt. Er is aangetoond dat de technologie en kennis (grotendeels) aanwezig is om een dergelijke campagne op een veilige manier uit te voeren. Dit zou een significante stap voorwaarts betekenen in het begrijpen van de verontreiniging in het sediment en de conditie van de munitie. Bovendien zou dit de heersende onzekerheden over (potentiële) alternatieve beheersscenario's voor de site sterk verminderen;
- DISARM heeft zowel nieuwe als bestaande gegevens en informatie samengebracht en gearchiveerd in een geïntegreerd geoportaal. Het is sterk aan te bevelen om **verder te investeren in dit datasysteem om de gegevens en resultaten** van toekomstige bemonsterings- en observatiecampagnes **adequaat te archiveren en te integreren**;
- Over het algemeen onderschrijven de resultaten van DISARM de tot nu toe gevolgde beheersaanpak om de Paardenmarkt onaangeroerd te laten en de toestand ervan te monitoren. Toch benadrukt de detectie van (zeer) lage concentraties aan munitiegerelateerde verbindingen op verschillende locaties van de stortplaats de noodzaak om **sneller te investeren in het dichten van enkele van de resterende kritieke kennishiaten** (bv. de lekkageflux en het lekkagevolume, effecten van mengsels van toxische verbindingen/chronische blootstelling, bioaccumulatie-/biomagnificatie-effecten, het potentieel van het stimuleren van biologische afbraakprocessen). Dit zal het mogelijk maken om de heersende risico's van de stortplaats verder te beoordelen en te verfijnen.

DISCLAIMER

Het huidige beleidsinformerende rapport is een eindproduct van het DISARM-project, gefinancierd door het Fonds voor Wetenschappelijke Onderzoek - Vlaanderen (FWO). Het rapport bouwt volledig voort op het uitgevoerde onderzoek en biedt een beknopt overzicht van de wetenschappelijke resultaten die binnen het kader van het project zijn behaald, namelijk een uitgebreide karakterisering van de Paardenmarkt munitiestortplaats. Hoewel het DISARM-project een geïntegreerde aanpak hanteerde, blijven relevante kennislacunes bestaan (bv. veiligheidsbedreigingen en mogelijke effecten op de menselijke gezondheid) die niet of slechts preliminair werden onderzocht in het project en als zodanig niet worden behandeld in dit document.

Contributor:
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What?

The primary objective was to determine whether there was freshwater submarine groundwater discharge (FSGD) beneath the Paardenmarkt munition dump site, accompanied by the goal of characterising this FSGD process.

Why?

Information on the presence of fresh groundwater under the Paardenmarkt is highly valuable as (1) freshwater conditions favorably influence the prevailing corrosion processes compared to saline water, and (2) it is important, from a health perspective, to assess if leakage of chemicals into freshwater lenses underlying the Paardenmarkt site could contaminate land-based groundwater reservoirs.

FRESHWATER DISCHARGE

How?

Two geophysical survey techniques were applied to investigate the salt-freshwater distribution in the pore water of the sediments underlying the Paardenmarkt:

- Continuous Resistivity Profiling (CRP – conducted offshore);
- Electrical Resistivity Tomography (ERT – conducted onshore).

Resistivity methods actively inject an electrical current in the water (CRP) or in the ground (ERT) to image the electrical resistivity of the sediments, which serves as a proxy for the salinity of the porewater.

Leap of knowledge

How much was already known about the research questions before the project started:

10% The presence of fresh or brackish water under the Paardenmarkt

Discharge characterisation **10%**

To what extent could the research question be answered:

100% The presence of fresh or brackish water under the Paardenmarkt

Discharge characterisation **75%**

Main outcomes

The study identified FSGD for the first time offshore Knokke-Heist up to 500 m offshore from the low-water line, corresponding with the southern limit of the Paardenmarkt, just outside of the polygon. The discharge showed substantial qualitative spatial variations in salinity, potentially caused by the heterogeneous nature of the sediments in the region. Freshwater reduces corrosion rates, however, the exact beneficial effects of FSGD on the corrosion process of the munition is currently impossible to determine due to diffuculties in the quantitative interpretation of the salinity variability based on the results of the resistivity methods. Lastly, it is important to note that the groundwater flow only occurs from land towards the sea, thus ruling out any risk of contamination from the Paardenmarkt of land-based freshwater lenses in the coastal zone.

Follow-up programmes

Paardenmarkt site

Study the causes of the observed high freshwater discharge heterogeneity around the Paardenmarkt site (sediment heterogeneity, impact of coastal construction works, impact of port of Zeebrugge) and its variable impact on corrosion. Building a groundwater model of the area, constrained to the geophysical observation, would allow to make more quantitative statements about the nature of the discharge (fresh or brackish water) and assess the vertical groundwater fluxes influencing the release of contaminants from the sediment to the sea.

Cross-area research

Recent droughts related to climate change have highlighted the vulnerability of (West) Flanders to water scarcity and the urgent need to find new management strategies, as water resources are scarce due to the absence of productive aquifers providing a substantial and sustainable source of water and the presence of fossil saltwater in shallow unconfined aquifers. In that context, freshwater lenses underneath dune belts do not only constitute groundwater reservoirs, but are also potential targets for the implementation of managed aquifer recharge and recovery. Therefore, the monitoring and quantification of FSGD will become even more important as an essential component of the water balance, given that it forms an indicator on the status of these groundwater reserves. This requires further study on the role of sediment heterogeneity on FSGD and the integration of geophysical data in shorebound groundwater models to quantify discharge fluxes. Additionally, information on the presence of fresh groundwater is highly valuable with respect to the installation of infrastructures in the coastal zone, as freshwater zones generate favorable conditions in terms of corrossion processes/rates compared to saline environments. A systematic mapping of the FSGD zones along the coast is therefore desirable.

Policy recommendations

As FSGD processes impact groundwater fluxes in the Paardenmarkt, which in turn are impacting contaminant migration in the sediment column, developing a groundwater model to quantify vertical fluxes is recommended.

> “ **The fresh groundwater discharge in the vicinity of the Paardenmarkt displays a flow from land towards the sea, ruling out any risk of contaminating land-based freshwater reservoirs.**

BURIAL DEPTH OF THE MUNITION

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What?

The aim was to obtain accurate burial depth information using innovative technologies, as well as information about the burial history of the munition and the total iron mass.

Why?

Burial depth information, including historical depth information, lies at the basis of any reliable risk assessment and is of vital importance for other research activities within the framework of the DISARM project (e.g. corrosion, ecological and explosion risk assessment). Furthermore, any potential (test) clearance operation of the Paardenmarkt dump site requires a sound knowledge of the total dumped (iron) mass. Prior to the project, magnetic data from 2013 provided an overview of the horizontal distribution of the munition, but burial depth information (estimated between 2 and 5 m) and iron mass estimation remained unreliable.

Leap of knowledge

How much was already known about the research questions before the project started:

20% Burial history

Current burial depth **25%**

To what extent could the research question be answered:

50% Burial history

Current burial depth **80%**

How?

Burial history

Based on 30 historical and recent hydrographic maps dating back to 1811, georeferencing and automated digitization techniques are employed to reconstruct the burial history of the munition dumpsite.

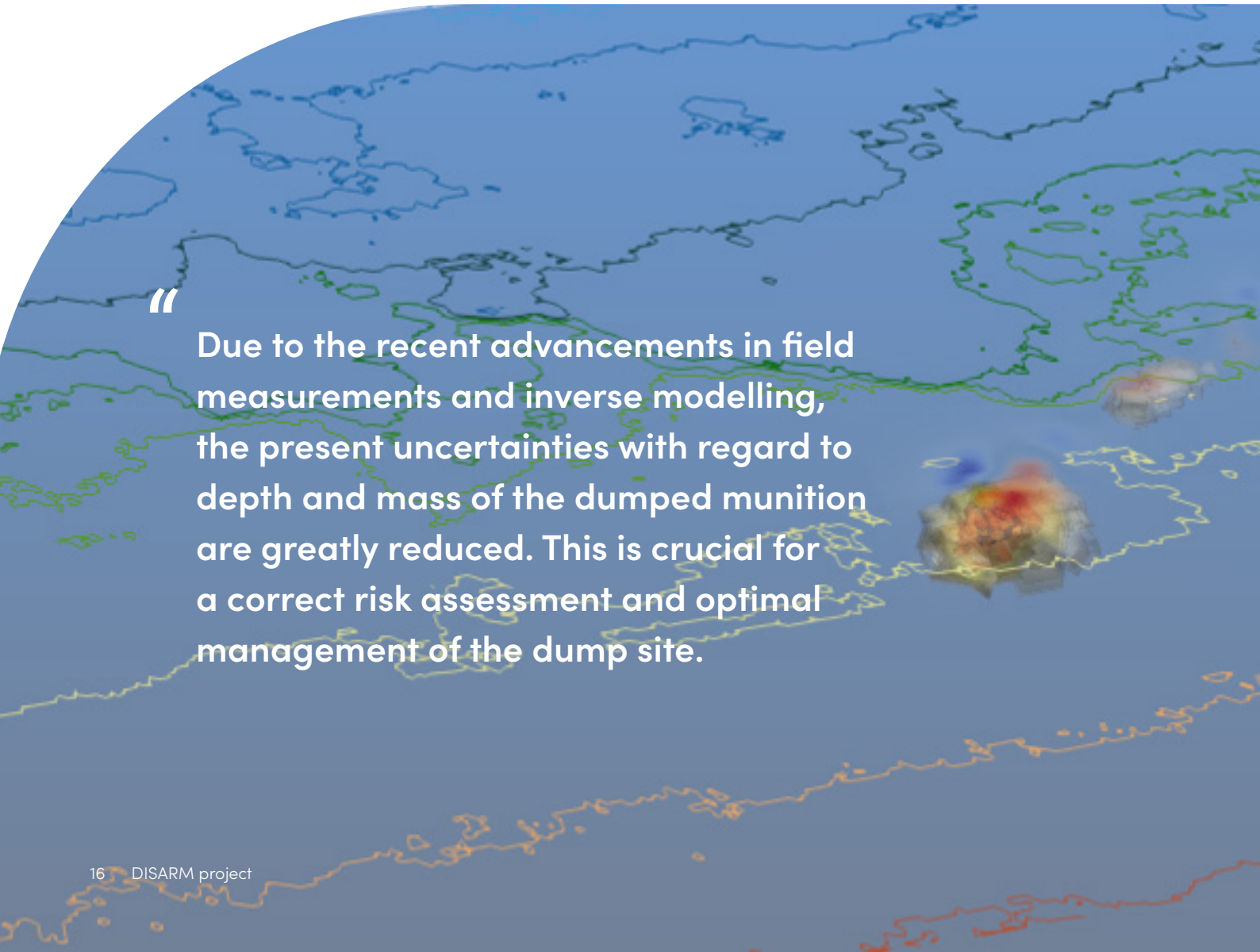
Current burial depth and mass estimation

- Proposed technique: deep sampling within the sediment using borehole techniques with built-in (electro)magnetic sensors (not executed – see chapter 'Road towards in depth sampling');
- Alternative option: high-resolution multi-sensor magnetometry complemented by 3D inverse modelling to improve the burial depth and iron mass estimation (executed).

Main outcomes

Burial history

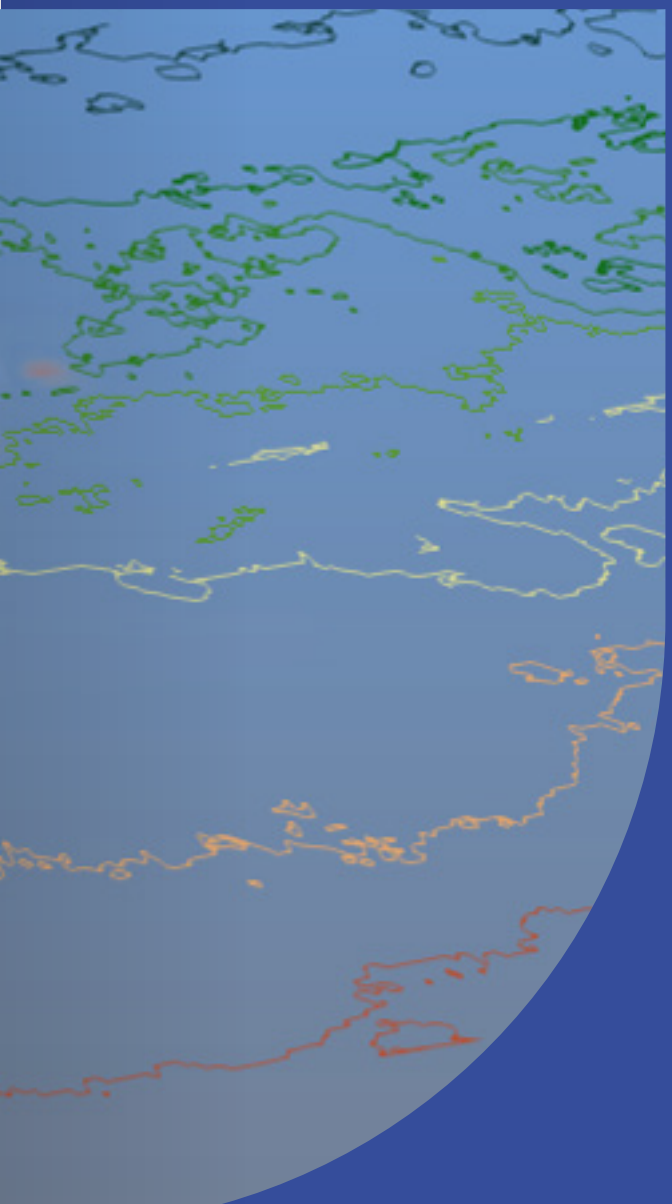
The analysis of historical hydrographic maps – resulting in depth maps, difference maps and some 3D seabed models – revealed that the seabed was subject to both large-scale erosion and sedimentation processes prior to the port extension in Zeebrugge (1978-1985). Therefore, it is deemed likely that the munition was periodically exposed on the seafloor, but no precise estimations can be given regarding the duration or extent of these exposure periods. Highly-dynamic morphological fluctuations of over 4 m were observed in the 19th century (before the munition dumping operation), while these fluctuations remained under 3 m in the first half of the 20th century. In the early 1970's, parts of the dump site area were subject to erosion, which may possibly explain the 'rediscovery' of munition in 1971-1972. After the seaward port extension in 1978-1980, changing current patterns resulted in pronounced sedimentation (up to 4-5 m at some locations) at the dump site and its surroundings, a process which resulted in a complete burial of all munition that seems to have largely stagnated since the early 2000's.



"Due to the recent advancements in field measurements and inverse modelling, the present uncertainties with regard to depth and mass of the dumped munition are greatly reduced. This is crucial for a correct risk assessment and optimal management of the dump site.

Current burial depth and mass estimation

Since conducting deep sampling within the sediment appeared unfeasible within the project's timeframe (see chapter 'Road towards in depth sampling'), high-resolution magnetometry complemented by advanced 3D inverse modelling was put forward as the alternative option. Detailed multi-sensor magnetic measurements were carried out in a small area (0.5 x 1 km) of the Paardenmarkt dump site. This was complemented by magnetic calibration measurements on WWI munition on land. The level of detail of the new marine survey data allows to map small isolated clusters or objects, but also enables to distinguish individual small clusters in areas that were previously identified as large single clusters. Inverse modelling of the new land and sea data resulted in mapping the subsurface distribution of the munition in unprecedented detail, including more reliable information on the burial depth and iron mass.



Follow-up programmes

Paardenmarkt site

In order to improve the inverse model, additional magnetic calibration measurements on land (with a higher data density and higher positioning precision), combined with magnetic susceptibility tests, are foreseen in 2024. This will ideally be preceded by a sensitivity analysis assessing the quality of the calibration data, including the influence of data resolution and remanence on the inversion process. This analysis will also help to better evaluate the potential of the offshore data.

Cross-area research

In the framework of the new EU HORIZON project 'MMineSweepER' (expected to start in fall 2024) the 3D inversion methodology will be upscaled for application to large(r) areas, which implies extending the inversion to an intelligent approach with automatic analyses. In addition, the methodology will be validated with other datasets (e.g. from the Baltic Sea) and preferably also datasets from controlled test sites which can act as a blind test case.

Policy recommendations

- Detailed high-resolution multi-sensor magnetic survey of the entire Paardenmarkt area;
- Inverse modelling of the new dataset (representative number of magnetic anomalies). This will not only allow to map the distribution of munition over the entire site in the highest detail, but also to get a good grip on the burial depth and total iron mass;
- Further identification and classification of the magnetic anomalies based on Machine Learning. This should help to discriminate between munition targets and other iron-containing objects (e.g. anchors);
- Improved positioning accuracy of the surface sediment sampling. The level of accuracy of the latest magnetic data and modelling results requires equally precise sampling in order to get a better grip on the spreading of contamination below the seafloor.

Contributors:

Flanders Marine Institute (VLIZ), Institute of Natural Sciences - OD Nature, Royal Military Academy (RMA), Defence Laboratories

What?

Develop a safe and precise sampling strategy within the sediment, at different depths and close to the munition (in collaboration with a specialised subcontractor – tender procedure), to provide insight into the spreading of contamination around the buried munition. Moreover these samples can also be used for further microbiological and ecotoxicological analyses.

Why?

As part of the standard monitoring of the Paardenmarkt, surface sediment samples are taken regularly. However, there is currently no insight into the extent to which the various substances are dispersed within the deeper sediment layers, and especially in the vicinity of the munitions (which are buried several metres below the seabed). Filling this knowledge gap would be of great added value and would significantly reduce the uncertainty on several other models and research lines developed in DISARM. Moreover, a thorough understanding of the contamination of the sediment surrounding the munition is an essential requirement to consider a substantiated (test) clearance. Also, any knowledge about the microbial communities in these potentially contaminated zones, which could be used in future management strategies (cf. bioremediation), is currently missing.

ROAD TOWARDS IN DEPTH SAMPLING

How?

Sampling within the sediment using highly specialised and innovative borehole techniques with built-in (electro)magnetic sensors was planned but not executed.

Main outcomes

An open dialogue tendering procedure on in depth sampling was set up by VLIZ. In order to minimise the risk of unwanted impact and to reduce the operational risks and the liability of VLIZ (as a non-profit organisation and the sole applicant of the permit), very strict technical criteria were applied for the tender. Although the technology and know-how seems to be largely in place, none of the tender participants were able to implement – within the lead time of the project – a solution that adequately met the terms of the contract. Still, the technical knowledge that was gained on the complex boundary/safety conditions and liability insurance aspects will be an important asset in any future government-led initiative involving sub-bottom disturbance at the Paardenmarkt dump site.

Leap of knowledge

How much was already known about the research questions before the project started:

0%

To what extent could the research question be answered:

50%*

*Knowledge leap in technical and legal aspects

As a result of the cancelled in depth sampling, the physical, biological and chemical characterisation of the dump site based on deep samples could not be done within the DISARM project and was therefore limited to the analysis of targeted surface samples (see chapters 'Monitoring techniques and early warning capacity' and 'Ecological (and human) risk of munition-related contaminants'). Additionally, an alternative approach was developed based on novel high-resolution magnetic measurements (at sea and on land) complemented by advanced 3D inverse modelling in order to obtain a better understanding of the burial depth and mass of the munition (see chapter 'Burial depth of the munition'). Combined with the targeted surface sampling, this already allowed - for the first time - to gain more insight on possible spreading of contamination below the seafloor.

Policy recommendations

The DISARM project advocates for a two-phase approach to address the challenge of in depth sampling at the Paardenmarkt site. Phase 1 entails conducting tests on sampling techniques within the sediment, focusing initially on a comparable area outside the dump site. This phase serves to refine and validate sampling methodologies. Upon obtaining positive results from phase 1, phase 2 will involve extending the testing efforts to the actual dump site area, facilitating more accurate assessment and management of potential risks associated with the munition dump site.

Follow-up programmes

Paardenmarkt site

The tender process has shown that the methodology (technically) for measurements and sampling within the sediment of the Paardenmarkt is technologically feasible. Depending on further planned investigations, the technical-legal knowledge gained in the course of this procedure can be used to optimise the risk framework and as such, open up new possibilities for in depth sampling within the Paardenmarkt sediment.

> "Conducting a safe measurement and sampling campaign within the sediment of the Paardenmarkt would mean a quantum leap in our understanding of the prevailing contamination. Moreover, it would greatly reduce the uncertainties concerning the different management scenarios.

STATE OF THE MUNITION AND CORROSION

Contributors:

Antwerp Maritime Academy (AMA), Ghent University - Center for Microbial Ecology and Technology (CMET), Flanders Marine Institute (VLIZ)

What?

The main goal was to assess the present and future state of the shell, cartridge casing and detonator of the Paardenmarkt munitions. This will in turn provide a deeper insight into the different prevailing corrosion processes, with a specific focus on the galvanic corrosion between the zamak detonators and the steel shells.

Why?

One of the major threats/uncertainties with regard to the contamination of the Paardenmarkt site is the condition of the steel shell and zamak detonators. Therefore, the assessment of their physicochemical state will provide important insights in the different corrosion processes occurring in the marine environment in aerobic as well as anaerobic condition.

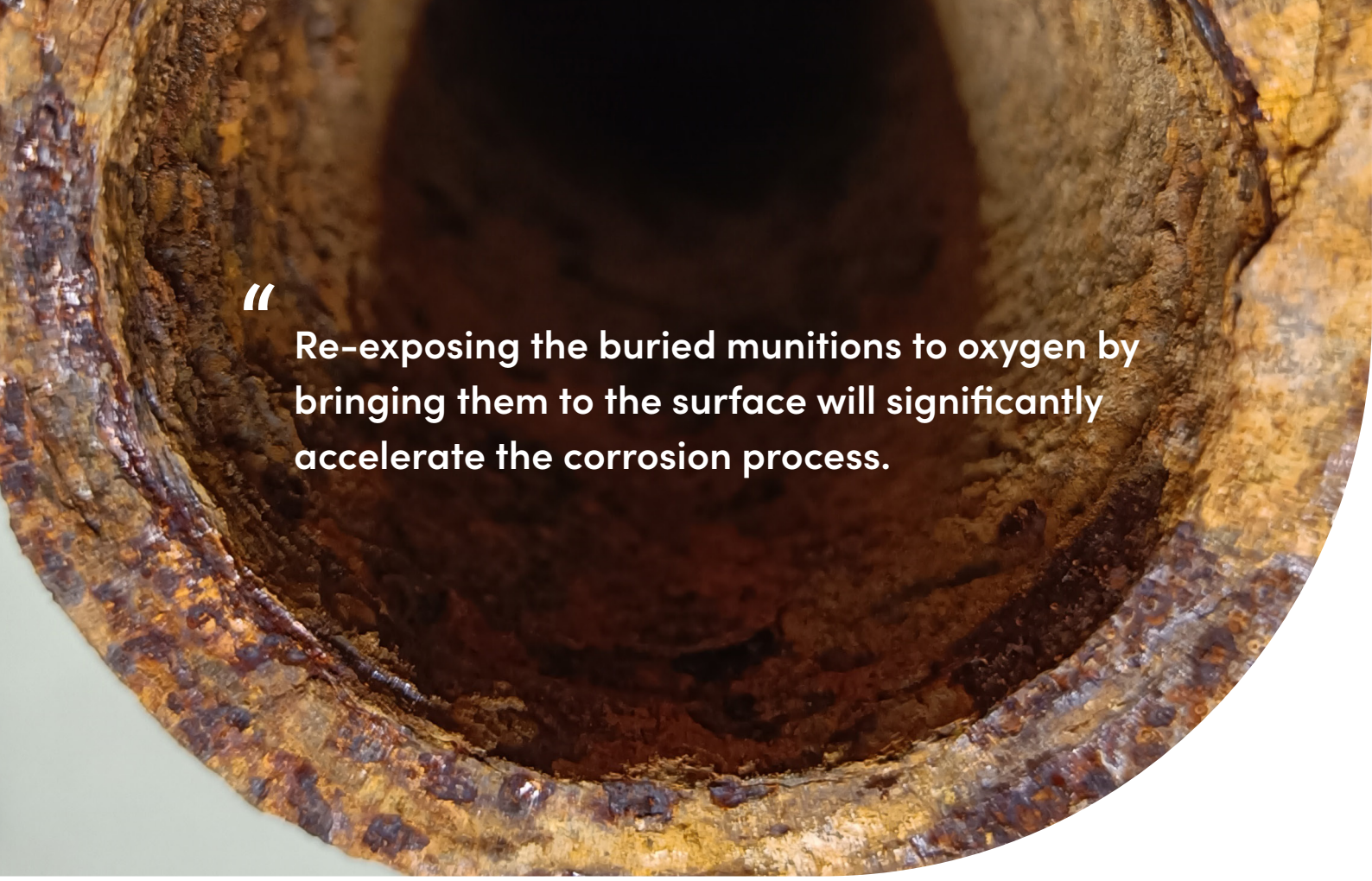
Leap of knowledge

How much was already known about the research questions before the project started:

0%

To what extent could the research question be answered:

25%



> Re-exposing the buried munitions to oxygen by bringing them to the surface will significantly accelerate the corrosion process.

The latter may in turn prove valuable for various economic sectors, such as the offshore wind sector, submarine pipeline construction, underwater heritage, etc.

How?

Since recovery of munition from the Paardenmarkt dump site is not allowed in accordance with current regulations, an experimental approach combined with innovative long-term corrosion modelling was deemed the best alternative. The experimental part included:

- Measurements of different WWI shell and cartridge casings obtained from a.o. museums and DOVO;
- Mesocosm experiments to analyse corrosion rates between 2 and 36 months using the weight loss method. These experiments also accounted for the influence of microbial communities (MIC) and salinity on the condition of the shell casings (the influence of hydrogen chloride will be assessed on lab scale);
- Studies and/or simulations of different types of corrosion (galvanic, (an)aerobic and inwardly chemical corrosion);
- Extrapolating the obtained results to 100 years using the validated multi-phase Melchers model.

Besides empirical testing, the galvanic corrosion process was also studied theoretically using formulas and techniques that are commonly used for cathodic protection by sacrificial anodes or impressed current. Comparison between these values and the experimental results will be interesting and useful. If the difference between both falls within acceptable limits, long-time testing can be avoided in the future.

Main outcomes

Corrosion is a complex process determined by various environmental parameters. Hence, the large variation of conditions (the availability of oxygen and the salinity of the water) and microbial activity in marine systems as the Paardenmarkt will further add to the complexity of the corrosion process. The overarching modelling effort capturing this variety is still ongoing. Ultimately, the main goal is to create a model which is able to predict long-term corrosion processes on munition shells in marine sediments. This model will be fed with the outcomes of mesocosm and lab studies, which already demonstrated that prevailing corrosion rates of zamak, brass and iron are quite slow (also on North Sea wrecks) compared to other regions in the world. Furthermore, specific attention was paid to the study of anaerobic galvanic corrosion between the zamak fuses and steel shell, a topic that has remained virtually unstudied to date. The methodology applied here may result in higher standards for future projects on this and other dump sites.

The model will require further refinement as additional information about the munition's construction becomes available. For example, galvanic corrosion at the zamak-steel interface should theoretically be expected to be very high. However, (1) the use of an isolating Sorel magnesium cement between detonator and shell and (2) the formation of natural concretion on the munition after 100 years of immersion in the North Sea water (analysis of WWI munition at Poelkapelle) may reduce the galvanic corrosion rate. This might also be a significant factor causing a notable disparity between the outcomes obtained in the test tanks and the actual conditions at the Paardenmarkt site.

Follow-up programmes

Paardenmarkt site

- Since no samples were taken close to the munition, many research questions on the local physicochemical sediment characteristics and the microbial effects on corrosion remain unanswered. In addition, there is a great deal of uncertainty about the chemical corrosion from inside out, the effect of temperature, the combined erosion-corrosion effect, the influence of burial depth (and the prevailing oxic/anoxic conditions) and the potential formation of concretions around the shells. Analysing the munition in situ (or at least being able to observe a number of the artefacts) is crucial to answering these questions and to validate the long-term corrosion model;
- Regarding the impact of microorganisms on the conservation state of the munition, it is not feasible to process all the soil and corrosion samples of the mesocosm experiments using the 16S rRNA sequencing method. Therefore, there is a need for a cost-effective, easier and faster analysis method, e.g. high-resolution melting curves. The research done in WP3 on steel coupons and soil samples has therefore to be further validated by follow-up projects;
- Another aspect hardly studied is the internal corrosion caused by toxic substances within the munition, which is currently impossible to study due to strict restrictions on the use of the toxic warfare substances in question. As a result, the study had to be simplified, only considering the influence of different concentrations of hydrogen chloride on the corrosion rate. Nonetheless, conducting a comprehensive kinetic study on the generation of corrosive products during the decomposition of the toxic contents constitutes a distinct project in itself.

Cross-area research

- An additional important aspect to be followed up concerns the fact that corrosion experiments mostly last for relative short periods, while the model for long-term corrosion of munition shells (predicting corrosion rate based on their burial characteristics) has added value towards the offshore industry;
- Lastly, further research is needed on the formation of concretions around the munition as the generation of this type of artificial layer could be an innovative and eco-friendly way of protecting subsea artefacts.

Policy recommendations

On the one hand, sediment samples close to the munition are needed to reduce the prevailing uncertainties on environmental parameters for the corrosion research on the Paardenmarkt. On the other hand, it should be mentioned that the current situation on the Paardenmarkt, where the munitions are buried beneath a few meters of North Sea sediment in an anaerobic environment, creates the lowest possible corrosion rates. When one re-exposes the munitions to oxygen by bringing them to the surface, the corrosion process will accelerate significantly. Hence, adequate dismantling facilities need to be in place before considering a test clean up.

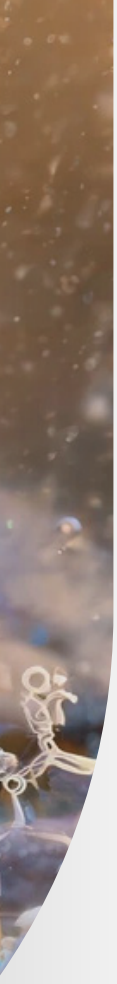
Contributors:
Ghent University - Center for Microbial Ecology and Technology (CMET), Institute of Natural Sciences - OD Nature

What?

Characterising microbial communities native to the Belgian part of the North Sea to detect and quantify microbial indicators that may lead to the development and application of highly efficient synthetic microbial communities (collaboromes) for the bioremediation of key contaminants.

Why?

A number of studies have indicated the potential of microorganisms isolated from groundwater or soil environments, to degrade toxic munition-related compounds and highlighted the degradation pathways. However, only a few studies have investigated the bioremediation capacity of microbial communities in marine systems. Generating key fundamental insights into the degradation of munition-related compounds by microbial communities can (1) prove to be an efficient indicator of munition-induced pollution and (2) serve as an efficient, cost-effective and low-risk solution to mitigate environmental pollution and the associated ecological and human health risks.



BIOREMEDIATION

How?

Novel lab experiments were set up in which the marine microbiome was exposed to a constant low energy flux and low concentrations of munition-related compounds to mimic the low concentration of pollutants detected at the contaminated site.

To enrich the novel degrader the marine microbiome was exposed to high concentration of munition-related compounds. Changes in the marine microbiome were detected by a state-of-the-art flow cytometry method developed by CMET and 16S Illumina sequencing analysis.

Main outcomes

The results demonstrated that the microbiome of the Paardenmarkt is highly diverse and that the insertion of certain microbial communities, such as *Methylophaga* and *Burkholderiales*, seems to be a promising solution to remediate TNT, mustard gas (Yperite) and Clark contamination. The following observations were made during the lab experiments:

- Rapid degradation of the munition-related compounds coupled to an efficient utilisation of toxic degradation metabolites by the enriched microbiome;
- A first-time observation of the biodegradation of the mustard gas metabolites 1.4-oxathiane and 1.4-dithiane;
- The discovery of novel microorganisms – *Methylophaga* and *Burkholderiales* – that can steer the complete removal of the munition-related compounds used for this experiment;
- Exposure to munition-related compounds resulted in changes in the flow cytometry-based fingerprinting of the microbiome which can indicate munition-induced pollution.

Leap of knowledge

How much was already known about the research questions before the project started:

10%

To what extent could the research question be answered:

75%

As such, these results allow for the use of microbial communities as an efficient indicator for biomonitoring and an early warning system regarding the spreading of contamination from buried munition in the central dump site area of the Paardenmarkt site. Furthermore, the results highlight the potential of the applied methodology for bioremediating toxic compounds in marine munition dump sites as the Paardenmarkt. For both applications, a TRL between 4-5 (technology validated in lab - technology validated in relevant environment) has been achieved in the DISARM project.

Follow-up programmes

Paardenmarkt site

The scientific progress made so far with regard to microbial communities and degradation pathways unlocks novel, efficient and cost-effective strategies with respect to dynamic (biological/environmental) monitoring as well as biological remediation of the Paardenmarkt dump site. Hence, this approach can be complementary to conventional chemical monitoring. In addition, this knowledge will contribute to further research efforts on the effects of microbial corrosion on munition, which in turn can facilitate the development of corrosion-resistant materials.

However, it's vital to acknowledge that even though key players in the degradation process have been identified, it remains imperative to gain a deeper comprehension of the interactions among various microbial populations and their distinct functional roles. This will ultimately enable the construction of collaboromes, facilitating targeted bioremediation efforts at sites such as the Paardenmarkt site. The next step has already been initiated, in which core (key degrader) and satellite (helper) members of the involved microbial communities will be isolated, using the robust methodologies of CMET.

Cross-area research

With the developed approaches, the intention is to expand the analysis of the microbial communities towards other munition dump sites or even shipwrecks to construct a microbial database that can be easily applied to detect the presence of munition in the marine environment.

> **"The DISARM research demonstrates the great potential of microbial communities as indicators for biomonitoring as well as bioremediators of toxic compounds at marine munition dump sites such as the Paardenmarkt.**

ECOLOGICAL (AND HUMAN) RISK OF MUNITION-RELATED CONTAMINANTS

Contributors:

Ghent University - Blue Growth Research Lab, University of Antwerp – ECOSPHERE, Institute of Natural Sciences - OD Nature, Ghent University - Center for Microbial Ecology and Technology (CMET)

What?

The assessment and modelling of the dispersion of potentially toxic munition-related compounds and the evaluation of associated ecological (and human) risks.

Why?

The main concern about the Chemical Warfare Agents (CWA), explosives and related compounds at the Paardenmarkt site is their leakage from the munition through the sediment layer into the overlaying water column, creating (potential) ecological and human health risks. Acquiring a better insight into the leakage and spreading process is crucial in case timely action is necessary. Furthermore, the effect assessment of mixtures of chemicals at concentrations relevant to the Paardenmarkt will allow for the further scientific underpinning of environmental criteria which are indispensable to develop early-warning indicators and cost-effective monitoring schemes.

Leap of knowledge

How much was already known about the research questions before the project started:

40%

To what extent could the research question be answered:

70%

How?

Within the DISARM project, the following research activities were undertaken:

- Examining the fate and toxicity of individual chemicals (including derivatives), basic mixtures and complex realistic mixtures at the Paardenmarkt site by tailor-made in-situ sampling (water column, sediment pore water, top layer sediment) and lab experiments;
- Fine-tuning and adaptation of the integrated COHERENS model (RBINS) to the Paardenmarkt site to simulate the transport of munition-related compounds. COHERENS has a hydrodynamic core complemented by several modules, such as a sediment transport and a pollutant transport module. The pollutant module considers non-conservative pollutants in the sense that they can shift between three phases: attached to the seabed sediment, attached to suspended sediment or a dissolved phase. The adapted model was subsequently applied to:
  - Map the pollution spreading for different scenarios of munition-related compound concentrations and current patterns under various combinations of tidal and meteorological conditions;
  - Assess the spatial and temporal extent of contamination in each scenario.

Main outcomes

The research succeeded in establishing a methodology capable of detecting munition-related substances at very low concentrations in sediment and water. The method can therefore be considered as a practical early warning system. The dispersion behavior of the munition-related contaminants was successfully modelled using the adapted, integrated (hydro - sediment - chemical) COHERENS transport model. As the model also takes into account the dilution and degradation of the contaminants in the water column, this allowed a good estimations of the spatiotemporal fate of the contaminants.

The results of the ecotoxicological research provided a better understanding of the effects of various munition-related chemicals on bacteria, copepods, algae and fish*. An environmental risk assessment was conducted using ecotoxicity data of the Paardenmarkt site and adhering to European ECHA guidelines. In this regard, the measured concentrations at the Paardenmark dump site are compared to safe concentrations (PNEC - Predicted No Effect Concentration) resulting in risk ratios (RQ). An RQ below 0.1 points at a negligible risk, values between 0.1-1.0 indicate a cause for concern (uncertainty) while above 1, a risk is established.

The results of the area-wide chemical monitoring of the Paardenmarkt between 2021 and 2023 indicate a widespread leakage of toxic compounds. In 85% of the sediment samples analysed between 2021 and 2023, explosives and related chemicals (E&RC) were detected, in 3% of these samples chemical warfare agents (CWA)&RC were observed. For the bottom water samples, E&RC was measured in 91% of the samples, while CWA&RC were detected in 4% of the samples over the period of 2021-2023. At the majority of the sampling locations, the risk was negligible, however, the measured concentrations of toxic compounds in a few samples are cause for concern (2% of the measured samples) or pose a risk for bottom-dwelling organisms (0.5% of the measured samples). Targeted sampling campaigns in 2019 and 2023 on locations where clusters of munitions could be expected based on earlier leakage detection or magnetic measurements further increased the share of samples where a cause of concern (15%) or risk (2%) for epibenthic organisms due to leakage of toxic compounds (E&RC and CWA&RC) was observed. If we zoom in on the targeted sampling campaign of 2023, CWA&RC were detected in significantly more sediment (17%) and bottom water (33%) samples compared to the area-wide sampling campaign of 2021-2023. However, it should be noted that the measurements point towards highly fragmented and variable contamination levels. It is envisaged, that once in the water column, these contaminants are subject to dilution and degradation.

*Because there is a lack of pertinent information, and the existing guidelines do not include *in vitro* data for the purpose of risk assessment, it was not possible to carry out a comparable risk assessment for human health.

Follow-up programmes

Paardenmarkt site

Currently, very little information is available on the possible chronic effects of the continuous leakage of small concentrations of munition-related contaminants on the environment and human health. Additionally, the potential impact of these releases on natural populations and biodiversity at the ecosystem level cannot be estimated based on current research results. On top of this, there are no actual observations to estimate the (dispersion) processes in the deeper (> 0.3 m) sediment layers, which are indispensable to get a more accurate picture of the actual leakages. This is an important gap in the current knowledge that should be addressed both in terms of sampling campaigns and in modelling effort.

Cross-area research

The current research allowed to deepen our understanding of the effects of munition-related chemicals on key aquatic species across different trophic levels. However, further (eco)toxicity data are essential for a more accurate assessment of the risks to marine organisms inhabiting the water column and sediment in the vicinity of the Paardenmarkt. Studies assessing the effects of chronic exposure to munition-related chemicals, focusing on sediment-dwelling species, are of particular importance since the munitions are buried in the seabed. Future research focusing on the bioaccumulation and biomagnification potential of munition-related chemicals across the marine food web, is necessary to estimate the likelihood of human long-term exposure via the consumption of contaminated seafood. While acute effects on human health are only observed at concentrations much higher than those previously detected in marine biota, further research is required to understand the chronic effects of these chemicals on human health, with a particular focus on organs directly involved in the digestive system.

In parallel with the assessment of the effects, continuous chemical monitoring of the dump site is essential for realistic exposure assessment. An integrated model incorporating both biogeochemical and ecotoxicological modules would be essential for quantifying the impacts of exposure in cases where experimental data are lacking. Carrying out biomonitoring campaigns, focusing on the effects on biodiversity, would provide insight into the impact of munition dump sites on the marine ecosystem.

Policy recommendations

The assessment of the impact and behavior of mixtures of chemicals at concentrations relevant to the Paardenmarkt by accurate in-situ sampling and modelling, now allows for improved scientifically-underpinned environmental criteria that can be applied as early warning systems and be considered cost-effective monitoring instruments. To further expand this knowledge and gain insight into the evolution of the leakages, it is crucial that the monitoring strategy for the water and sediment is maintained. How the current leakages affect biodiversity and the functioning of the ecosystem should be further investigated, for example, based on eDNA techniques. If these results can be compared with non-polluted regions, this could provide vital information about the extent to which chemical munition dump sites pose a risk to humans and the environment.

> **“ Adhering to the EU standards for environmental risk assessment, the research shows that munition-related risks cannot be excluded considering the widespread leakage of contaminants. This finding emphasises the necessity to close critical knowledge gaps to mitigate potential risks and thus preserve the integrity of the local and regional marine environment.**

Contributor:
Royal Military Academy (RMA)

What?

A model for the explosion risk assessment of the munition dump site at the Paardenmarkt was developed based on the (semi-)quantification of different potentially hazardous events and their effects.

Why?

Given the proximity of the port of Antwerp-Bruges (location Zeebrugge) and the densely inhabited coast of Knokke-Heist, it is important to scientifically underpin the risk of an accidental explosion under different scenarios, along with its scale and impact.

RISK ASSESSMENT EXPLOSIVES

How?

- A risk identification, analysis and evaluation was developed using a case-specific Failure Mode Effect Analysis (FMEA). Kinney's scale scoring matrix was used to rate the FMEA, assigning numerical scores to hazards based on their likelihood and severity (low score = no action required, high score = immediate cessation of all activities);
- Next, the impact of compound aging was examined using recovered explosives from WWI. Chemical analysis determined the energetic content, while sensitivity to friction and impact was compared between aged and non-aged samples. Subsequently, performance assessment was conducted on one of the aged samples;
- Finally, an underwater test campaign was conducted, including small-scale and medium-scale tests in laboratory and field settings, respectively. Pressure sensors were utilised to measure both underwater and above-water (aerial) shock waves. Additional small-scale experiments included burying explosive charges in sand to measure the propagation of shock waves in water. These experiments aimed to evaluate the reduction of aerial shock wave pressure, relevant for munitions buried beneath the seabed. Numerical simulations were performed to develop predictive tools for future assessments.

Leap of knowledge

How much was already known about the research questions before the project started:

30%

Potential explosion impact after mechanical impact was previously estimated by Missiaen and Henriet (2010)

To what extent could the research question be answered:

90%

Main outcomes

The aged compounds contained the expected explosive substances and they exhibited similar energy release, ignition, and sensitivity characteristics, both for friction and impact, when compared to non-aged pure explosives. Furthermore, performance tests showed no discernible differences between aged and non-aged compounds, as evidenced by 100-year-old TNT detonating in a manner indistinguishable from that of recently produced TNT.

Because the munitions are buried beneath a layer of sand, the aerial shock wave resulting from an accidental explosion of (part of) the munitions at the Paardenmarkt will be significantly attenuated. Therefore, this shock wave would not be comparable to the shock wave produced by the same mass of explosives if detonated in the open air. The large reduction in pressure leads to a large reduction of effects and consequently also a reduced risk linked to an explosion. The fact that the munitions are most likely not armed or equipped with an arming system, is also a factor that reduces the risk. Numerical simulations and experimental data generally showed similar trends, although absolute values sometimes differed.

- Ageing in sea water could not be studied, but should be in the future. However, it is not expected to influence the risk analysis providing the munition is not broken or completely corroded;
- Since the medium-scale tests resulted in less reproducible results, mainly for the measurements of the shock wave in the air, more experimental research to fully understand these observations is necessary;
- The investigation of the explosion impact of munition in different conditions and at different burial depths in subsea sediments (burial vs. non-burial effects) is also worth further investigating.

Cross-area research

The state of corrosion has an important influence on the risk assessment. Corrosion likely increases the possibility of detonation by sympathy, can lead to dissolution of explosives in the sea water (leading to a smaller amount of explosive in the munitions) and might lead to modified sensitivity in the ignition systems (if present). In addition, when less energy is required to break a corroded casing, more energy is available in the shock wave.

Moreover, the type of sediment will influence the effect of a buried charge, another topic that needs to be taken into account for a more precise calculation of the effects of an explosion. If more information could be gathered on the distribution and type (chemical or conventional) of the dumped munitions in the seabed, that would significantly influence the risk analysis by better quantification of the risk of detonation by sympathy and of the total mass of explosives that could be triggered.

Follow-up programmes

Paardenmarkt site

- The 'detonation by sympathy' of buried munitions needs further research, as this will give an idea of the likelihood that the accidental explosion of one munition leads to the explosion of other munitions;

Policy recommendations

The semi-quantitative risk analysis determined that, at present, there is virtually no risk of harm to humans resulting from a potential explosion of the munition buried at the Paardenmarkt site, except for persons present at the dump site. Furthermore, the 100-year-old explosives do not differ in sensitivity to friction or impact and still detonate with the same properties as non-aged explosives, meaning that they do not seem to become unstable.

> "
>
> **The aged explosives of the Paardenmarkt site retain their explosive properties, but the danger to humans is virtually non-existent.**

MONITORING TECHNIQUES AND EARLY WARNING CAPACITY

Contributors:
Defence Laboratories, Institute of Natural Sciences - OD Nature

What?

Lower the detection/quantification limits for toxic munition-related compounds to enable monitoring of the evolution of the pollution and determine the migration in the sediment.

Why?

Improved detection techniques with lower threshold values for dangerous munition-related compounds (e.g. Clark, mustard gas (Yperite), TNT) will allow to make a more complete and therefore more reliable monitoring of the Paardenmarkt dump site. These new developments pave the way towards an early warning system for the site that enables timely action in case an enhanced leakage of toxic compounds would occur.

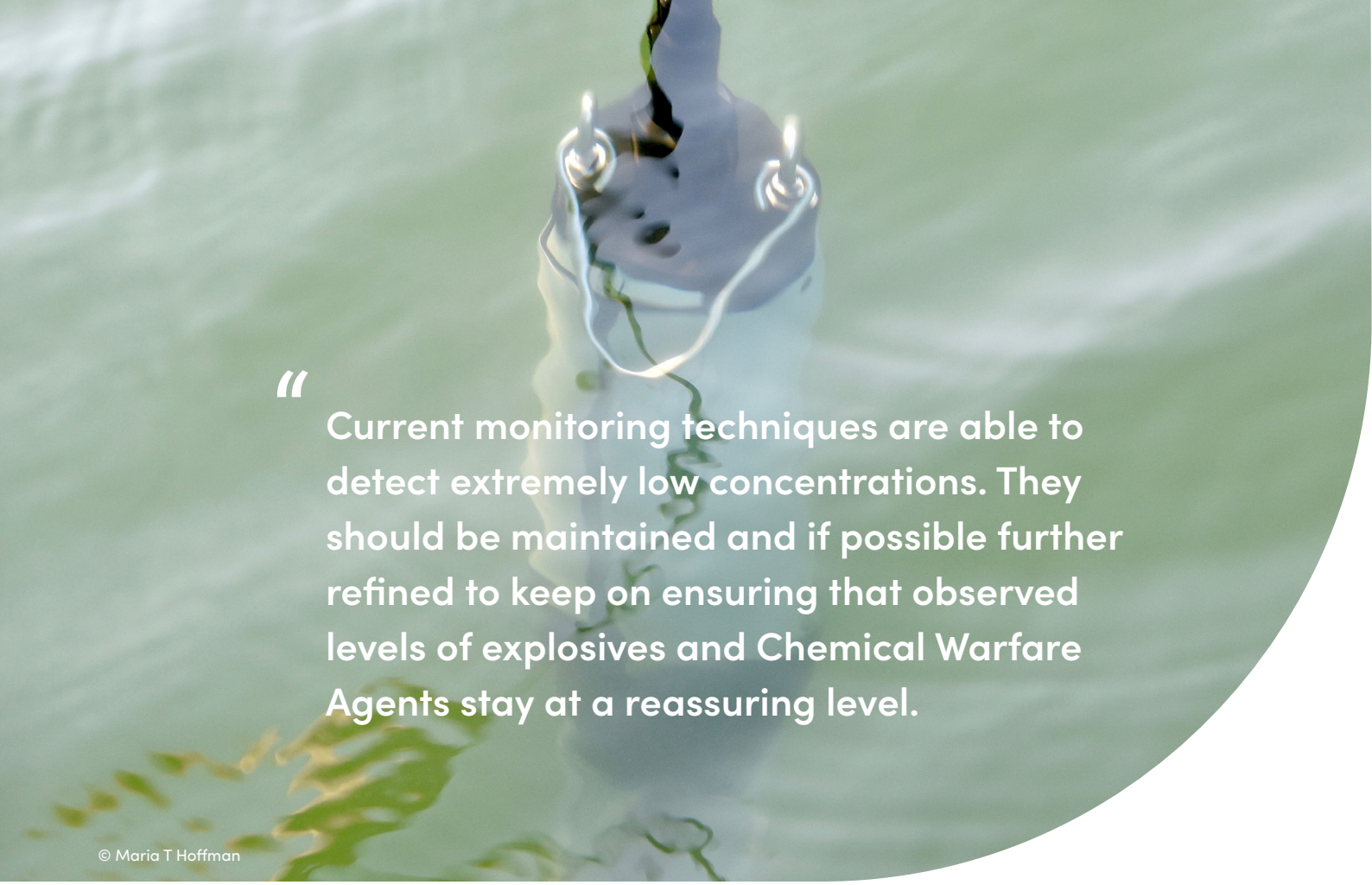
Leap of knowledge

How much was already known about the research questions before the project started:

30%

To what extent could the research question be answered:

85%



> "Current monitoring techniques are able to detect extremely low concentrations. They should be maintained and if possible further refined to keep on ensuring that observed levels of explosives and Chemical Warfare Agents stay at a reassuring level.

© Maria T Hoffman

How?

As part of the DISARM project, the following research activities were conducted:

- Chemical analysis methods were improved by using high-end mass spectrometric techniques (tandem mass spectrometry, high resolution mass spectrometry)
- Sample preparation was adapted to handle higher sample volumes in order to improve detection limits;
- The (potential) ecotoxicological and human health risks for different scenarios of toxic munition-related compound concentrations and current patterns was explored under various combinations of tidal and meteorological conditions;
- The bioaccumulation and biodegradation potential of microbial communities for bioremediation purposes was evaluated;
- A unique and safe technique for sediment sampling close to the munition under the seafloor was developed but not executed (see also chapter 'Road towards in depth sampling').

Main outcomes

In the context of chemical monitoring, methodological advancements have enabled very sensitive detection of munition-related compounds in the top-layer sediment and the overlaying water column. Regarding TNT and its degradation products, the LOQ (Limit of Quantification) is currently in the sub-ng/L range for seawater, the low ng/L range for porewater and 10 ng/kg range for sediments, categorising it way below lowest PNEC (Predicted No Effect Concentration). Hence, this novel chemical monitoring capacity qualifies as an early-warning system.

To monitor traces of Chemical Warfare Agents (CWA), markers of mustard gas (Yperite) and Clark were identified and targeted analytical methods now allow to use these compounds in an early warning system (detection limits well below 1 µg/kg and far below the PNECs). In addition, the number of warfare target compounds that can be detected has been expanded (e.g. picric acid and some dichloroarsines). The new (low) threshold values and analytical techniques for explosives and CWA thus represents a crucial instrument for improved monitoring and the establishment of thresholds for environmental legislation. Moreover, it is anticipated that this improved detection ability of minimal concentrations will over time provide more reliable information on the actual evolution of the contamination on the Paardenmarkt site.

With respect to the biomonitoring capacity, a new flow cytometry-based monitoring method was developed within DISARM, enabling the dynamic monitoring of marine munition dump sites. This method allows to swiftly detect changes in the marine microbiome when exposed to munition-related compounds. Thus, along with chemical monitoring, microbiological monitoring is an additional opportunity to identify toxic leakage of munition from the dump site as well as the associated environmental impact. This discovery unlocks important perspectives for future innovative environmental monitoring.

Follow-up programmes

Paardenmarkt site

- The project consortium holds and will remain to hold close contact with the competent federal authority to maximally incorporate these new techniques in future monitoring schemes of the Paardenmarkt dump site;
- Improving chemical monitoring techniques will enhance opportunities for targeted screening. One can consider two options: (1) monitoring based on multiple, widespread sampling points covering the entire site versus (2) the monitoring of a few closely-spaced sampling points in the most suspicious areas. The trade-off between both options will depend on practical considerations (e.g. available resources) as well as on the analyte considered (e.g. warfare agents compared to explosives);
- A better understanding on how biomonitoring using microbial communities can be combined with biodiversity monitoring using molecular techniques such as eDNA may be a promising way forward;
- Improving detection limits for arsenic compounds will require superior instruments.

Cross-area research

To assist DISARM partners working on biodegradation and toxicity, a fast screening method to determine the concentration in their samples was developed for TNT and its degradation products as well as for selected degradation products of Yperite (mustard gas) and picric acid. This proved to be adequate for assisting both toxicity analysis (as it allowed the quantification of actual exposure concentrations and to assess fate and distribution in the actual setup) and for the identification and characterisation of the microbiome developed under specific conditions (by precise determination of the observed concentration as the microbiome develops, checking both the degradation pathway and kinetics). The interesting observations would benefit from further research, as the microbiome is not yet fully characterised, and newly discovered species might use different pathways.

Policy recommendations

Recent methodological advancements and discoveries have significantly enhanced monitoring capabilities at the Paardenmarkt site, leading to the development of an effective and internationally applicable early warning system. However, the current analytical infrastructure has reached its limits, necessitating investments in high-resolution instruments, particularly for quantifying arsenic compounds. Moreover, potential pathways for enhancing on-site monitoring include utilising molecular techniques like eDNA for assessing biodiversity impact, deploying in-situ passive samplers, in depth sampling, online smart monitoring, as well as remote autonomous underwater vehicles and sensors. While the monitoring of explosives and CWA meets the necessary standards for an early warning system, continuous systematic monitoring of the Paardenmarkt area is vital to detect any spatiotemporal variations that may require attention. Such an early warning system should also include a coupled hydrodynamic-sediment-pollutant transport model that would allow to forecast and provide spatiotemporal maps of the transport of the munition-related compounds.

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