

SUMMARY REPORT

SERDP and ESTCP Workshop on State of the
Science and Research and Development Needs
for Assessing the Environmental Risk of
Conventional Underwater Military Munitions
SERDP Project ER-2341

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SERDP WORKSHOP REPORT

STATE OF THE SCIENCE AND RESEARCH AND DEVELOPMENT NEEDS FOR ASSESSING THE ENVIRONMENTAL RISK OF CONVENTIONAL UNDERWATER MILITARY MUNITIONS (UWMM)

SERDP Project ER-2341

MAY 23 – 24, 2018, WASHINGTON NAVY YARD, WASHINGTON, DC

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TABLE OF CONTENTS

Table of Contents	i
List of Tables	iii
List of Figures	iv
Acronym List	vi
1.0 Introduction	1
2.0 Underwater Munitions Overview and Historic and Geographical Perspective.....	4
2.1 Overview	4
2.2 Global Historic and Geographic Perspective.....	6
2.3 U.S. UWMM Sites	7
3.0 State of the Science	9
3.1 Overview of Release and Corrosion	9
3.1.1 Release into Surrounding Environment.....	9
3.1.2 Corrosion.....	13
3.2 Tracing the Fate of the Energetics Released in Temperate Marine Ecosystems.....	15
3.3 Sampling Water, Sediment and Biota	22
3.3.1 Water Column Direct Sampling	23
3.3.2 Water Column Passive Sampling	24
3.3.3 Sediment Sampling	25
3.3.4 Sediment (Porewater) Passive Sampling	26
3.3.5 Biota Sampling	27
3.4 Chemical Analysis of Water, Sediment and Biota Samples	28
3.4.1 Water	28
3.4.2 Sediment	29
3.4.3 Biota	30
3.5 Toxicity of MC to Aquatic Biota.....	31
3.5.1 Toxicity to Aquatic Autotrophs.....	31
3.5.2 Toxicity to Aquatic Invertebrates.....	32
3.5.3 Toxicity to Tadpoles and Fish.....	33
3.5.4 Toxicity of Spiked Sediment to Aquatic Invertebrates and Fish	34
3.5.5 Summary of Recent Studies	35
3.6 Toxicity of MC to Corals	35
3.6.1 Methods.....	36
3.6.2 Toxicity of Munitions Compounds to Coral Fragments and Coral Cells	39
3.6.3 Photo-enhanced Toxicity of TNT.....	40
3.6.4 Species Sensitivities to 2,6-DNT	40

3.6.5	Effect of MC on the Coral Endosymbiotic Dinoflagellate, <i>Symbiodinium</i>	41
3.6.6	Correlation of Cell-based Assays with Responses of Intact Coral Fragments.	41
3.6.7	Conclusions	41
3.7	Bioaccumulation and Toxicity of Energetic Compounds in Terrestrial Biota and Relevance to Aquatic and Wetland Environments	45
3.8	Removal Challenges/Blast Risk	47
4.0	Site Studies.....	50
4.1	Overview of MC in Water, Sediment and Biota at UWMM Sites	50
4.1.1	MC in the Water Column	50
4.1.2	MC in Sediment.....	53
4.1.3	MC in Biota.....	55
4.2	Ecological Risk Assessment Considerations for UWMM Sites	57
4.2.1	Comparison of Water Concentrations with Toxicity Benchmarks.....	58
4.2.2	Comparison of Sediment Concentrations with Toxicity Benchmarks	61
4.2.3	Conclusions regarding risk posed by MC in sediment	66
4.2.4	Evaluation of Risk Using MC Concentration in Biota	66
4.3	Underwater Munitions Constituents Vieques Naval Training Range (Puerto Rico)	67
4.3.1	Background	67
4.3.2	Research.....	67
4.3.3	Results/Lessons Learned.....	68
4.4	Remedial Action Decision Making for Navy Jackson Park Underwater Munitions Site.	69
4.4.1	Conclusions	77
4.5	Investigating Sea-disposed Munitions at Deep Water Sites Near Oahu, Hawaii	77
4.5.1	Results	82
5.0	Stakeholder Challenges and Perspectives	84
5.1	Shaping Community Understanding of the Risks of Underwater Munitions: The Importance of Sound Science and Effective Communication.....	84
5.1.1	Introduction	84
5.1.2	States and Territories of the USA	84
5.1.3	Non-Governmental Organizations and Business, Case Study: Offshore Wind Farms, Germany	85
5.1.4	Case Study: Vieques, Puerto Rico	86
5.1.5	Conclusions and Recommendations.....	88
5.2	Role of Natural Resource Trustees in Munitions Response.....	89
5.2.1	Ecological Characterization of the Marine Resources of Vieques	90
5.2.2	Underwater Unexploded Ordnance Demonstration Project	90
5.2.3	Coral Reef Restoration Demonstration Project	90
5.2.4	Land and Fiddler Crab Study	91
5.2.5	Other Activities	91

5.3	Navy Munitions Response Site Challenges and Management.....	92
6.0	Group Discussion and Recommendations	96
7.0	References	103
8.0	Appendix	116
8.1	Workshop Agenda.....	116
8.2	Attendee List	118

LIST OF TABLES

Table 3-1.	Environmental conditions found in different corrosion zones.....	14
Table 3-2.	List of munitions compounds and breakdown products tested.....	38
Table 3-3.	Summary of no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) across all coral experiments. Blanks indicate that testing was not performed.	43
Table 3-4.	Summary of lethal (LC) and effect (EC) concentrations across all coral experiments. DMF = Data model failed. Blanks indicate that testing was not performed.	44
Table 4-1.	Detection frequency and range of measured concentrations of MC in the water collected at Halifax Harbor (Halifax, Canada).....	51
Table 4-2.	Detection frequency and concentrations of MC in the water column near UWMM as measured by passive samplers and grab samples at grid locations as measured by grab samplers at the Isla de Vieques Bombing Range site (PR).	52
Table 4-3.	Detection frequency and concentrations of MC in the biota sampled from Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA) Operable Unit 2 and Operable Unit 1.....	55
Table 4-4.	Maximum water column concentrations of selected MC at several field sites.	60
Table 4-5.	Maximum concentrations (noted as 95% upper confidence limit, where indicated) of MC in sediment samples collected at UWMM sites, number of samples, number of samples exceeding benchmark, and HQs calculated using sediment benchmark values SQB _{low} and SQB _{high} . Values in bold indicate HQ>1 (rounded to the unit).	63
Table 4-6.	Sediment quality benchmarks (SQB) for MC (from Lotufo et al. 2017).	64
Table 4-7.	Time series munitions compounds detected in marine biota, Ostrich Bay, WA.....	75

Table 5-1. Public perception of impacts from cleanup, including terrestrial detonations, and existence of munitions in underwater areas at Vieques compared to scientific findings	87
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LIST OF FIGURES

Figure 2-1. Examples of munitions in U.S. waters. Note variable condition and degree of encrustation, which may affect dissolution of MC to the surrounding environment.....	4
Figure 2-2. Explosive train.....	5
Figure 3-1. Comparison of measured TNT concentration vs predicted TNT concentration using the Shell Model release function under flume conditions for Scenario 2.	12
Figure 3-2. Design of the MC ¹⁵ N isotope tracer experiments.	16
Figure 3-3. Time series concentrations of TNT, RDX, and detected organic derivatives in the four aquaria..	17
Figure 3-4. Time series parent MC concentrations in flow-through mesocosm experiments where an initial pulse of MC was followed by continued delivery of MC to achieve a steady state supply.	19
Figure 3-5. Cumulative distribution of isotope tracer in TNT mesocosm experiments.	21
Figure 3-6. Cumulative distribution of isotope tracer in RDX mesocosm experiments. More organic matter equates with less persistence of RDX and derivatives.	22
Figure 3-7. HEL glass-teflon coral culture system. A) Experimental system fabricated with all glass and Teflon® parts, the lighting system uses custom-made light-emitting diode fixtures. B) NOAA glass-teflon coral culture system..	37
Figure 3-8. HEL and NOAA's coral fragment dosing systems. A) HEL- replicate 200 mL glass beakers fitted with individually controlled Teflon® airlines. B) HEL - close-up of individual treatment replicate. C) NOAA dosing system.	37
Figure 3-9. Current investigation/remediation tools used or being evaluated for underwater MEC.	48
Figure 3-10. Examples of current and future remediation tools, including views associated with BIP before (A) and after (B) remediation, various forms of LUC (C,D), waterjet cutting technology (E), and use of (F) advanced manipulators and ROVs.....	49
Figure 4-1. Ostrich Bay, WA – Current Jackson Park Housing Complex (JPHC) on the left side...	70
Figure 4-2. Former Naval Ammunition Depot (NAD) Puget Sound, circa 1959.....	71

Figure 4-3. Geophysical Prove-Out of Marine Magnetometer Survey, Ostrich Bay, WA. A pontoon boat towed the sensor platform, which is submerged 7 ft below the surface.	72
Figure 4-4. Spatial (left) and vertical (right) locations of Recovered DMM in Ostrich Bay.	73
Figure 4-5. Typical condition of recovered DMM by divers in Ostrich Bay, WA.	73
Figure 4-6. Dissolution timeframe estimated for an 8” munition using the Shell Model (Wang et al. 2013).	76
Figure 4-7. HUMMA survey areas (UH and Environet 2016).	79
Figure 5-1. Map showing former eastern and western components of the former Atlantic Fleet Weapons Training Area.....	87
Figure 5-2. Conceptual site model for MRP sites.	94

ACRONYM LIST

3,5-DNA	3,5-dinitroaniline
ADNT	Aminodinitrotoluene
AOC	Area of concern
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration factor
BIP	Blow-in-Place
BRAC	Base Realignment and Closure
CA	Chemical agent
CDOM	color dissolved organic matter
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COPC	Chemicals of Potential Concern
CSM	Conceptual site model
CWA	Chemical Weapon Agent
DDT	Dichlorodiphenyltrichloroethane
DEGDN	Diethylene glycol dinitrate
DETN	diethylenetriamine trinitrate
DGT	Diffusive gradients in thin
DL	Detection limit
DMM	Discarded military munitions
DNAN	2,4-dinitroanisole
DNA	Deoxyribonucleic acid
DNB	1,3-dinitrobenzene
DNP	dinitrophenol
DNT	dinitrotoluene
DNX	Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DoD	U.S. Department of Defense
DOI	U.S. Department of Interior
DON	Dissolved organic nitrogen
DS	Desantnyy Sudno (English translation: Landing Vessel)
EC	Effective concentration
ECD	Electron capture detector
EPA	Environmental Protection Agency
ESA	Endangered Species Act
ESL	Ecological screening level
ESTCP	U.S. Department of Defense's Environmental Security Technology Certification Program
EVA	Ethylene-vinyl acetate
FFA	Federal Facilities Agreement
FUDS	Formerly Used Defense Site

FUI	Follow-up investigation
fVNTR	Former Vieques Naval Training Range
fVNTR-BSS	Bahia Salinas del Sur Lagoon at the former Vieques Naval Training Range
GC	Gas chromatography
GC/ECD	Gas chromatography with an electron capture detector
GC/MS	Gas chromatography–mass spectrometry
GIS	Geographic Information System
GP	General purpose
HD	Distilled sulfur mustard
HEL	Haereticus Environmental Laboratory
HLB	Hydrophilic lipophilic balance
HMS	Her Majesty's Ship
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocane
HOV	Human occupied vehicle
HPLC	High-performance liquid chromatography
HPLC-UV	High-performance liquid chromatography–ultraviolet detection
HQ	Hazard quotient
HUMMA	Hawaii Undersea Military Munitions Assessment
IM	Insensitive Munition
IRP	Installation Restoration Program
JPHC	Jackson Park Housing Complex
Kow	Octanol-water partition coefficient
LC	Lethal Concentration
LC50	Median lethal concentration
LC-MS/MS	Liquid chromatography-Mass spectrometry and Liquid Chromatography-Tandem Mass Spectrometry
LIA	Live Impact Area
LOC	Level of concern
LOD	Limit of detection
LOEC	Lowest observed effect concentration
LOQ	Limit of quantitation
LRL	Laboratory reporting limits
LUC	Land use controls
MBB	multibeam bathymetric
MC	Munition constituents
MD	Munitions debris
MDL	Method detection limit
MEC	Munitions and Explosives of Concern
MIDAS	Munitions Items Disposition Action System
MMRP	Military Munitions Response Program
MNR	Monitored Natural Recovery

MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MR	Munitions response
MRF	Munitions Response Forum
MRP	Munitions Response Program
MRS	Munitions Response Sites
MRSP	Munitions Response Site Prioritization Protocol
MS	Mass spectrometry
NAD	Naval Ammunition Depot
NATO	North Atlantic Treaty Organization
NAVFAC NW	Naval Facilities Engineering Command Northwest
NCP	National Contingency Plan
NG	Nitroglycerin
NHB	Naval Hospital Bremerton
NIWC	Naval Information Warfare Center
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOEC	No observed effect concentration
NQ	Nitroguanidine
NT	Nitrotoluene
NTO	3-nitro-1, 2, 4-triazol-5-one
OPA	Oil Pollution Act
ORD	Office of Research and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR Convention
OU	Operable unit
PAM	Pulse-amplitude modulated
PES	Polyethersulfone
PETN	Pentaerythritol tetranitrate
POCIS	Polar organic chemical integrative samplers
PR	Puerto Rico
PREQB	Puerto Rico Environmental Quality Board
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RI	Remedial investigation
ROV	Remotely operated vehicle
RP-HPLC-UV	Reversed-phase high-performance liquid chromatography with a UV detector
SERDP	U.S. Department of Defense's Strategic Environmental Research and Development Program
SI	Site inspection

SLRA	Screening-level risk assessment
SPAWAR	Space and Naval Warfare
SPE	Solid-phase extraction
SPM	Suspended particulate matter
SPME	Solid-phase micro extraction
SQB	Sediment quality benchmarks
SSC	SPAWAR Systems Center
SSS	Side-scan Sonar
TAT	2,4,6-triaminotoluene
TEM	Transmission electron microscopy
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TNX	Hexahydro-1,3,5- trinitroso1,3,5-triazine
TSERAWG	Tri-Service Environmental Risk Assessment Working Group
TWA	Time-weighted average
UH	University of Hawaii
UHPLC-ESI-MS	Ultra-high performance liquid chromatography – electrospray ionization – mass spectrometry
UK	United Kingdom
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
UV	Ultra violet
UWMM	Underwater military munitions
UXO	Unexploded ordnance
WA	Washington State
WW	World War

1.0 INTRODUCTION

The manufacturing of explosives and munitions has left contamination of terrestrial and aquatic systems. Activities such as the loading, assembling, and packing munitions; the use of munitions and explosives in testing, training, and combat; and accidents involving munitions and explosives presents a continuing source of contamination. Many active and former military installations have ranges and training areas that are adjacent to water environments such as ponds, lakes, rivers, estuaries, and coastal zones. Explosives-loaded munitions and fragments of explosives and munitions remaining following failed or incomplete detonations are often found in aquatic habitats next to these sites. In addition, disposal of munitions at sea was considered an acceptable option with large quantities discarded into the ocean following the World Wars. The Department of Defense (DoD) discontinued this practice in 1970. The DoD has identified more than 400 sites totaling more than 10 million acres potentially containing munitions in underwater environments.

Underwater unexploded ordnance (UXO)¹ and discarded military munitions (DMM)², collectively referred to as underwater military munitions (UWMM), present challenges due to both explosive blast (safety) considerations and potential ecological and human health impacts resulting from the release of munitions constituents (MC)³ to the aquatic environment. UWMM have the potential to corrode, breach, and leak MC into aquatic environments. Growing concern by public and regulatory communities has resulted in costly risk assessments and could lead to resource-intensive remediation efforts.

¹**Unexploded Ordnance (UXO)** — Military munitions that: (A) have been primed, fuzed, armed, or otherwise prepared for action; (B) have been fired, dropped, launched, projected, or placed in such a manner as to constitute a hazard to operations, installations, personnel, or material; and (C) remain unexploded whether by malfunction, design, or any other cause. ([10 U.S.C. §101\(e\)\(5\)](#)).

² **Discarded Military Munitions (DMM)** — Military munitions that have been abandoned without proper disposal or removed from storage in a military magazine or other storage area for the purpose of disposal. The term does not include unexploded ordnance, military munitions that are being held for future use or planned disposal, or military munitions that have been properly disposed of, consistent with applicable environmental laws and regulations. ([10 U.S.C. §2710\(e\)\(2\)](#))

³ **Munitions Constituents (MC)** — Are any materials originating from UXO, DMM, or other military munitions, including explosive and non-explosive materials and emission, degradation, or breakdown elements of such ordnance or munitions. ([10 U.S.C. §2710\(e\)\(3\)](#))

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) actively fund research, demonstration, and validation of projects that lead to an improved and concise understanding of the fate and environmental risks of MC that are released from munitions present at UWMM sites. Accurately identifying ecological risks associated with military-unique compounds has been a Program priority since inception.

Key SERDP and ESTCP investments have been to (1) provide a comprehensive review document, database, and modeling tools to address the environmental risks posed by MC (Lotufo et al. 2017, [SERDP Project ER-2341](#)), (2) develop advanced tools capable of detecting low levels of MC that leak from underwater UXO ([Rosen et al. 2017, [ESTCP Project ER-201433](#); Belden et al. 2016, [SERDP Project ER-2542](#); Vlahos et al. 2016, [SERDP Project ER-2539](#)), and (3) quantify the pathways and rates of MC processing in three typical coastal ecotypes (Tobias, 2019, [SERDP Project ER-2122](#)). Details about these projects and other mentioned in this report are available at the SERDP and ESTCP website (<https://www.serdp-estcp.org>) by conducting a search using the project number.

SERDP and ESTCP hosted a meeting in 2009 to assess the status of various elements needed to evaluate risk associated with munitions in the underwater environment. The main objective of that meeting was to evaluate the adequacy of modeling capability and data sources needed to make defensible risk-based decisions regarding underwater munitions. A summary of the meeting discussion documenting capabilities that currently exist and identifying where advancements are needed has been published as a white paper (SERDP 2010).

As a follow-up to the 2009 workshop, an expanded technical workshop bringing together a total of over 50 DoD site managers, scientists, regulators, and stakeholders was conducted in May 2018 at the Washington Navy Yard in Washington, DC. The workshop was planned and organized under [SERDP Project ER-2341](#). The goal of the workshop was to assess progress, questions, and continuing challenges related to understanding and managing environmental risk associated with UWMM. The workshop, as well as this report, focused on conventional munitions, which are those containing conventional explosives, smokes and pyrotechnics. Chemical weapons and risk to human health were not a focus of the workshop. The workshop goals included: 1) reviewing existing scientific evidence regarding environmental risks posed by UWMM; 2) discussing relevant uncertainties associated with these risks, and 3) evaluating known and foreseen challenges associated with obtaining site-specific MC concentrations in various matrices (water column, sediment, and biota) to validate risk conclusions at UWMM sites. Of particular importance for the workshop was to provide a venue for open exchange of ideas among participants with varying backgrounds and views, and to use this exchange to identify and prioritize pathways towards effective management as well as identifying remaining research

gaps. The workshop agenda and list of participants is provided in the Appendix and workshop presentations are available upon request.

2.0 UNDERWATER MUNITIONS OVERVIEW AND HISTORIC AND GEOGRAPHICAL PERSPECTIVE

2.1 Overview

Conventional munitions occur in underwater environments worldwide because of 1) use in military training, and testing, 3) use during combat, 3) accidents, and 4) their intentional disposal at sea or in other water bodies. For the purposes of this report, conventional military munitions present in underwater environments are referred to UWMM; Figure 2-1.



Figure 2-1. Examples of munitions in U.S. waters. Note variable condition and degree of encrustation, which may affect dissolution of MC to the surrounding environment.

MC are the explosive and non-explosive materials and emission, degradation, or breakdown products associated with military munitions. This includes organic energetic compounds, metallo-organic explosives, and the metals and other materials of the munitions body. Organic energetic compounds used in legacy munitions can be grouped according to general molecular structure. Generally, these include: nitroaromatics (2,4,6-trinitrotoluene, TNT; 1,3,5-trinitrobenzene, TNB; dinitrotoulene, DNT; 2,4-dinitroanisoie, DNAN; picric acid; tetryl), nitramines (hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX), nitrate esters (pentaerythritol tetranitrate, PETN; nitroglycerin, NG; diethylenetriamine trinitrate, DETN), triazoles and tetrazoles (e.g., 5-aminohydroximoyl-2-hydroxytetrazole). Organometallic explosives include lead azide, lead styphinate, and mercury fulminate. Many of these groups of chemicals share patterns in chemical physical properties that can be used to help predict fate and transport. Energetics as a group are strong oxidizers, most

often reduced in wet, anaerobic environments predominantly via microbial processes. They are often not very water-soluble nor fat-soluble and tend to form crystals.

Munitions are designed for safe handling and storage and to reliably function when desired (e.g., to withstand rough handling, difficult and long-term storage without detonating prematurely but functioning as designed when employed). This is achieved with an explosive train consisting of energetic materials arranged according to decreasing sensitivity and increasing potency. A primary explosive, the most sensitive material, is mixed with other ingredients in the priming composition to adjust the sensitivity of the mixture to the desired property, such as percussion or heat. The priming composition is used in small quantities in the initiator because of its sensitivity. A booster is used to either detonate a bursting charge that is too insensitive to be detonated by the relatively weak initiator, or to ensure complete detonation of the main charge (Figure 2-2). The booster contains a larger quantity of less sensitive but more powerful secondary or high explosives. The main or bursting charge is the least sensitive material (also a secondary explosive) and is the bulk of the explosive charge (Army 1990 –TM 9-1300-214, Military Explosives).

Secondary explosives differ from primary explosives in several major ways. Small, unconfined charges (one to two grams) of secondary explosives, even when ignited, do not transfer easily from burning or deflagration to detonation. The shock required for ignition is much greater for secondary explosives than for primary explosives (Army 1990 –TM 9-1300-214, Military Explosives).

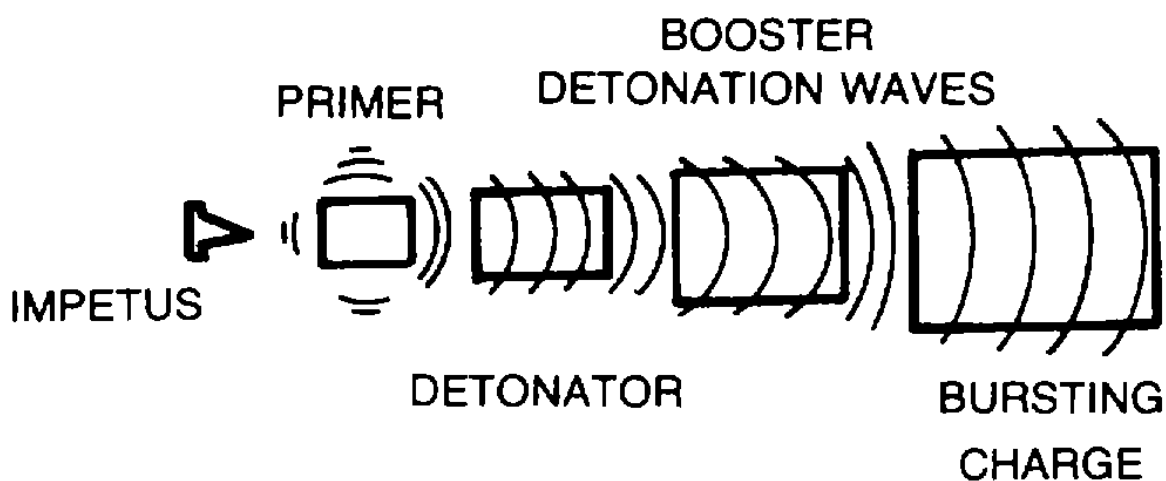


Figure 2-2. Explosive train.

Relatively insensitive common organic high explosive compounds used as the main charge formulation include nitroaromatics such as TNT, and nitramines such as RDX and HMX. Other

explosive compounds have been used historically, such as tetryl (trinitrophenylmethylnitramine) and ammonium picrate, but TNT, RDX, and HMX represent a major portion of munition material present in terrestrial and aquatic environments (USEPA 2012). Sensitive metallo-organic compounds used as initiators for detonation of secondary or tertiary explosives include fulminates, azides, and styphnates of mercury, lead, and silver. Components of driving bands, casings, and fuzes of conventional munitions may include both ferrous and nonferrous components such as steel, brass, copper, aluminum and zinc (Craig and Taylor 2011; Beck et al. 2018).

2.2 Global Historic and Geographic Perspective

Many countries (e.g., United States, United Kingdom (UK), Russia, Germany, Italy, France, Canada) manufactured large quantities of munitions that were filled with explosives or chemical agents for use in the First World War (WW I), and more so for use in the Second World War (WW II) (Carniel et al. 2019). Some of these munitions were disposed of to eliminate stockpiles of excess, obsolete, unserviceable, or captured munitions. After World War II, the U.S., France, the Soviet Union, and the United Kingdom relied heavily on sea dumping to dispose of confiscated German weapons and Japan also dumped chemical materials off its coastline (Pfeiffer 2016). Those DMM generally do not have all the components required for them to function as designed and have not gone through an arming sequence. These are items that are usually taken from storage, removed from packaging, and disposed while still in their storage configuration (e.g., fuse not installed). Until the 1970s a significant fraction of excess, obsolete, or unserviceable munitions and explosives of concern (MEC)⁴ was disposed in the ocean or in large lakes, because that was considered safe and inexpensive (Carniel et al. 2019; Maser and Strehse 2020). Intentional disposal of MEC in the ocean was practiced until promulgation of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter in 1972 (Oslo Convention, and 1975 London Convention of the same name) (Carton and Jagusiewicz 2011). In the United States, the Marine Protection, Research and Sanctuaries Act of 1972, also known as the Ocean Dumping Act, implements the requirements of the London Convention. DoD ceased sea disposal of munitions in 1970. Munitions that have been prepared for use (i.e., they have

⁴ **Munitions and Explosives of Concern (MEC)** — This term, which distinguishes specific categories of military munitions that may pose unique explosives safety risks, means: UXO, as defined in 10 U.S.C. 2710 (e) (9); DMM, as defined in 10 U.S.C. 2710 (e) (2), or MC (e.g., TNT, RDX) present in high enough concentrations to pose an explosive hazard. ([Title 32 CFR 179.3](#))

been fused) and either did not function as intended (e.g., duds) or were used as intended and are awaiting the needed stimulus to function (e.g., magnetic influence mine awaiting metal to come in close proximity) are known as UXO. Since UXO are complete, they are more likely to function and present a greater explosive hazard than DMM. UXO represents an additional relevant source of underwater munitions stemming from combat early in the 20th century as well as early (e.g., U.S. Revolutionary War) and recent conflicts (e.g., Persian Gulf War). MEC consists of UXO, DMM, and MC which pose an explosives safety hazard (e.g., could detonate or deflagrate). A common method used for *in situ* UWMM disposal is the intentional detonation initiated by placing a small donor charge on the munitions in order to initiate an explosion of the main charge. This procedure is referred to as “Blow-in-Place” (BIP) or “Blast-in-Place” (Maser and Strehse 2020). Along with spontaneous detonation described in marine UWMM disposal sites (e.g., Ford et al. 2005), BIP often result in an incomplete (low-order) detonation, leaving substantial quantities of the explosive material in the environment (NATO 2010).

Historically, large quantities of munitions have been disposed of in the oceans and in large lakes. As examples, an estimated 1.6 million metric tons were dumped in the North Sea off the coast of Germany (Strehse et al. 2017); 300,000 tons were dumped in the Baltic Sea (Botcher et al. 2011), in excess of 1 million tons were dumped in Beaufort’s Dyke (Irish Sea; Callaway et al. 2011), and 168,000 tons in the Skagerrak Fjord in the northeastern Atlantic (Koch and Ruck 2009); approximately 1 million tons were disposed of in Canadian waters, including one shipwreck with an estimated 80,000 tons (Long 2011); approximately 8,200 tons of ammunition waste were dumped into some Swiss lakes (Estoppey et al. 2019). At least 148 dumpsites are spread from Iceland to Gibraltar, conventional munitions were discarded at 78% of the sites (Craig et al. 2019). In the Pacific, a number of islands have legacy underwater conventional munitions contamination remaining from combat operations during WW II and post war dumping (Francis et al. 2011). Wrecks of munitions-laden ships are also a major source of UXO in ocean environments (Aker et al. 2012) as more than 3,800 WWII era shipwrecks are present in the East Asian-Pacific region alone, many loaded with UXO (Monfils et al. 2006). The location and quantity of marine UWMM are generally poorly documented.

2.3 U.S. UWMM Sites

In the United States, munitions are present at numerous current and former DoD sites encompassing millions of acres. Many active and former military installations have ranges and training areas that include adjacent water environments such as ponds, lakes, rivers, estuaries, and coastal ocean areas. Within the Formerly Used Defense Sites (FUDS) program alone, the Army Corps of Engineers (USACE) has identified more approximately 230 sites with watered areas totaling about 5 million acres potentially impacted by munitions. Most of this acreage is

comprised of tidal sites of over 10,000 acres. Only about 19% of sites are over 10,000 acres but they make up about 97% of the total acreage.

The U.S. Navy and U.S. Marine Corps' Munitions Response Program (MRP) includes an additional 57 sites containing munitions. The inventory sites date back to the 18th century with some were used as recently as the 1990s. Munitions were fired or disposed of using various methods at numerous underwater sites. Ranges and targets include coastal defense sites, island targets, ranges that were previously land targets and were flooded, and littoral training areas. Currently, the most accurate references on range and site locations include FUDS reports, the Munitions Response Site Inventory in the Defense Environmental Programs Annual Report to Congress (<https://www.denix.osd.mil/arc/>), service historical offices, and nautical charts. The level of location accuracy for munitions from mobile firing points, bombing ranges, and disposal sites are more varied than fixed firing points. Historical disposal site information often provides only general locations and, when positions are provided, they are typically only accurate to the nearest minute, potentially complicating any attempt to locate the cited items. The most up-to-date data on locations and quantities of disposal sites is found in the Fiscal year 2009 Defense Environmental Programs Annual Report to Congress (www.denix.osd.mil). The FY09 Report to Congress identified 70 sea disposal sites for conventional munitions, some of those were also disposal sites for chemical warfare material.

3.0 STATE OF THE SCIENCE

3.1 Overview of Release and Corrosion

3.1.1 Release into Surrounding Environment

When undissolved MCs (e.g., still contained within a munition) are introduced into the aquatic environment, they are not immediately released; environmental releases only occur after the munition is breached by corrosion or mechanical breakage. Breaching can occur either through explosion, mechanical breakup on impact or through corrosion. UXO can be breached due to explosive stresses experienced during firing the round or on impact, resulting in MC release from either a low-order detonation (fully exposed to environment) or from hole or cracks in the round. Therefore, if the munitions remain intact, it is assumed that no chemicals are released to the environment, although Rodacy (2001) reported the presence of TNT in the vicinity of apparently intact UWMM. Since the munitions will typically corrode or breach slowly, it is likely that their contents will be released gradually until totally depleted. Breach size (i.e., shell casing hole size) is assumed to be a function of time in the instance of corrosion. Understanding the condition of munitions and their potential to breach via corrosion will help characterize the potential for energetic fill material that will transfer to the environment (Wang et al. 2013). After a breach, the MC release rate can be explicitly expressed as a function of the following five parameters: ambient current speed, hydrodynamic mixing coefficient, size of the breach hole, cavity radius inside the shell, and dissolution rate of MC from the solid to aqueous phase inside the shell (Wang et al. 2013). Release of MC fully exposed following BIP or spontaneous detonation will be a function of dissolution rate of solid MC from the solid to aqueous phase, ambient current speed and hydrodynamic mixing coefficient. Once released into the environment, the MCs are subject to fate and transport processes, which are discussed later in this report. When the shell is buried in sediment, fate and transport of MC released from the shell would be slowed, occurring on a time scale much longer than the modeled transport in the water column (Wang et al. 2013). MC transport through sediment surrounding a buried, breached shell is influenced by the presence of naturally occurring organic matter (Wang et al. 2013).

From a source characterization and exposure perspective, we need to know the potential magnitude of MC release from an ensemble of breached munitions that might be present at a site. At a given site, there may be many types of munitions in many different breach states, all releasing MCs at differential rates. Because of safety and environmental challenges associated with disturbing and handling the munitions *in situ*, high uncertainty exists for empirically assessing release key parameters such as how many and which items are breached, and the characteristics of the breach and of the fill inside, or the integrity of biofouled or buried items. For breached munitions, release is best addressed using models that take empirical and semi-

empirical distributions of munitions and combine them with parameters that control the release of MCs under the conditions at a given site.

The Shell Model (Wang et al. 2013, [SERDP Project ER-1453](#)), defines the estimation of the mass of MC (e.g., TNT, RDX, HMX and/or their breakdown products derived from their military compositions), in both quantity and form (i.e., chemical species), that is released from the breached shell into the water column and sediment (Wang et al. 2011, 2013). The Shell Model provides a way to quantify the fundamental processes that govern the MC release from a single shell, which can then be applied to an ensemble of shell types and conditions at a site. These fundamental processes are described by physical and chemical properties that ultimately define the total magnitude and rate of MC released into the surrounding environment for scenarios of interest. Scenarios of interest included UWMM that have a small breach hole that is (1) unburied, lying on top of sediment, or (2) entirely buried in sediment, or a munition with a fully exposed large breach hole or no breach hole such as that found in a low-order detonation with (3) exposed solid energetic material released directly to the underwater environment. For scenarios 1 and 2, the release through a breach in a munition casing can be determined by the following five key parameters: (a) the start and growth of the breach or the hole (expressed as the radius of the hole); (b) the radius of the cavity formed due to loss of mass released from inside the shell; (c) the chemical property (dissolution speed) from solid to aqueous phases of the MC inside the shell casing); (d) the outside ambient current to which the casing hole is exposed; and (e) mass of MC remaining inside. For scenario 3, low-order detonation contamination, dissolution speed, outside ambient current, and mass of MC available need to be considered as an extreme case where a breach is infinite in size. The Shell Model applies the MC release rate function, a function of the five listed variables (1 to 5 above), as the process descriptor that dictates the release rate of MC from the munition casing. The Shell Model is not a computer code but provides a means whereby the release function can be calculated deterministically for scenarios in which above parameters are known.

Originally validated analytically, and then numerically through simulation using Fluent (a computational fluid dynamic model), the Shell Model has also recently been validated empirically. A recent study (Lotufo et al. 2019) investigated the release of TNT and RDX from Composition B fragments under two realistic exposure scenarios in a large flume with flow set at 15 cm/s. Scenario 1 represented the release of MC from fully exposed Composition B and Scenario 2 represented release through a small hole, simulating a breached munition. The simulation employed a surrogate munition (155 mm replica of rubber composition) that had been cut down the centerline longitudinally, resulting in two ½ munitions with a flat underside that when placed on the floor of the flume would simulate a partially buried munition with half of its cylindrical projectile surface protruding above the sediment. For each ½ surrogate munition, recessed holes were machined into them for Composition B placement, to specifications dictated

for each scenario described above. This flume experiment (Lotufo et al. 2019) conducted under [ESTCP project ER-201433](#) (Rosen et al. 2017a), presented a unique opportunity to compare empirically-determined and predicted release rates. For Scenario 1, MC release was determined for fully exposed Composition B, without dependence on a breach hole. The dissolution rates for TNT and RDX from a Composition B source matrix into saltwater empirically-determined by Lynch et al. (2002) were used. For Scenario 2 release of MC from Composition B was through a small hole, simulating a breached munition. The Shell Model was used to ascertain what combination of breach hole size (radius) and internal cavity radius (simulating already dissolved MC) would provide a measurable concentration of TNT in the fixed flume volume, with remaining functional parameters dictated by the test conditions in the flume during MC release.

Measured concentrations in the water revealed that release of TNT and RDX from Composition B through a small hole was approximately ten times lower than from exposed Composition B, demonstrating the strong influence of exposure to flow on release. A comparison of predicted TNT concentration by the Shell Model release function to the measured total TNT compounds (TNT + 2-amino-dinitrotoluene (2-ADNT) + 4-ADNT) concentration in the flume for Scenario 2 is shown in Figure 3-1. Not only was the predicted TNT release within the same order of magnitude, but also showed good agreement, with only an approximate 3-4-fold difference observed over the course of the 13-day experiment. It is clear that there are other factors, perhaps related to the surface area of the Composition B source used in the experiment, contributing to the experimental release that the model does not capture adequately, but fortunately the predicted values are slightly over-predicted, i.e., conservative compared to experimental.

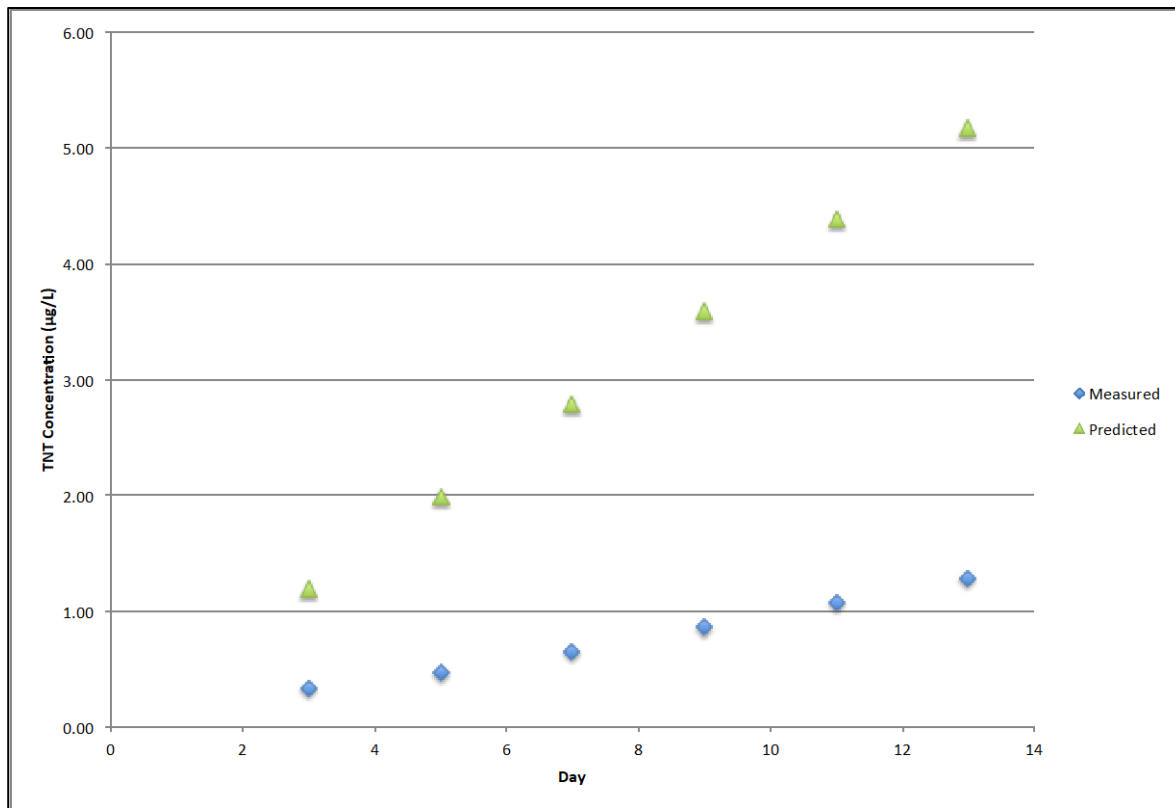


Figure 3-1. Comparison of measured TNT concentration vs predicted TNT concentration using the Shell Model release function under flume conditions for Scenario 2, showing a 3-4X difference.

A methodology was recently developed to extend the Shell Model to address a large number or distribution of breached shells at a site. One can use the Shell Model deterministically if discrete data are known for the parameters that govern the release. Alternatively, the Shell Model can use distributions or ranges of values for the parameters and estimate the release probabilistically. As presented in detail in Lotufo et al. (2017), distributions were assigned for parameters for which data was available such as breach hole size, radius cavity and current velocity. When the mass release rate function, developed for a single shell, is implemented for multiple shells, the number of shells for each shell type also needs to be prescribed, either deterministically or probabilistically. When multiple variables are prescribed probabilistically, each with its own distribution function, predictions would require a large number of calculations so that the variables with a probability distribution can be adequately sampled. For example, in previous efforts during the Shell Model study, the Monte Carlo method was used to perform simulations with 10,000 calculations conducted for each scenario. However, simulation results from the 10,000 calculations did not show a noticeable difference from the results of 1,000 calculations.

Relatively few sites exist with sufficiently robust characterization of munitions distributions. Using the limited site-specific data available for Bahia Salinas del Sur Lagoon at the former Vieques Naval Training Range (fVNTR-BSS). Sufficient knowledge about munitions at the site was derived via numerous site characterizations and diver verifications of site munitions. Release of MC was modeled using the Monte Carlo method to provide a probabilistic estimate of the release function distribution F (single munition) and the total site release function distribution F' (F applied to the distribution of munitions at the site) for TNT-filled Mk 82 munitions at fVNTR-BSS. Results from 1,000 trials were not significantly different compared to results from 10,000 trials, an observation also reported during the original Shell Model effort (Wang et al. 2011).

Using conservative assumptions about the volume of water at the site, the concentrations of TNT from this particular distribution predicted a conservative steady state concentration of 0.74 ng/L. A site-wide survey of contamination indicated that TNT is present at fVNTR-BSS below the detection limit of 4 ng/L except for one out of 15 sites where the concentration was 10 ng/L (Rosen et al. 2017a). Therefore, the probabilistic Shell Model correctly predicted the magnitude of contamination at the site. Finally, in the context of exposure characterization, the Shell Model can be coupled with fate and transport models for a site to evaluate what-if scenarios and assist with collection of appropriate site data.

3.1.2 Corrosion

As time progresses, metal objects resting on the seafloor rust and are subject to chemical and mechanical erosion. At some point, metal munitions casings will corrode to the point that there is direct contact between seawater and the MC. In the marine environment, the corrosion of metals is a complex process, mediated by a variety of electrochemical, environmental, and microbiological processes including the time DMM is exposed to the marine environment, the type, quality and thickness of materials used in construction, the availability of dissolved oxygen, seafloor current velocity, and the degree of burial within seafloor sediments Silva and Chock (2016). An overview of electrochemical corrosion processes, biotic contributions to corrosion, mineralization induced by bacterial activity in the marine environment are provided by Silva and Chock (2016).

Corrosion is dependent both on spatial and temporal variables associated with the environment where the UWMM resides. Most studies have focused on site-level corrosive processes that can be generalized, which are dictated by properties such as materials, salinity, temperature, dissolved oxygen, and mobility (e.g., Rossland et al., 2010; MacLeod, 2016; Jurczak and Fabisiak, 2017). Prediction of corrosion rates by those parameters do not account for the “micro” or localized corrosive behaviors that are present on each discrete munition. Different behaviors may be present at different locations on each munition and are related to a variety of factors such as

material properties and morphologies, features of each of these local microenvironments at the munition surface, and exposure during the course of its lifetime in the water to those microenvironments under differential conditions found in different corrosion zones (Table 3-1). This leads to a broad distribution of corrosion behaviors and high uncertainty when attempts are made to model the process. Each of these microenvironments might reside in different corrosion zones corresponding to different environmental corrosion conditions. Note that the zones are from seabed to atmosphere, differentiated by potential for biologically mediated corrosion, localized chemical environment, including dissolved oxygen, contaminants, geochemistry, light conditions, and physical processes such as sediment scouring. Munitions have been found in all of these zones and may reside in more than one over a long period of time.

Table 3-1. Environmental conditions found in different corrosion zones.

Zone	Typical Corrosion Conditions
Atmospheric	Oxic, no biofouling/bacterial, above seawater > above land
Splash zone – above water	Oxic, no biofouling/bacterial
Tidal/subtidal	Oxic (high), differential tidal vs. subtidal, some biofouling/bacterial, plant fouling, oil/contaminants
Shallow/littoral – near surface/shore	Oxic (saturated), variable conditions, current velocity, sediment, contaminants, biofouling/bacterial, plant fouling (photic zone)
Deep ocean	Oxic (low, Pacific primarily), no plant fouling (below photic zone), temperatures lower (low at continental shelf depths, 1-4°C deeper depths)
Sediment-seawater interface	Sediment scouring (shallow tidal or deep, current velocity dependent), oxic to anoxic (depth dependent)
Sediment	Varied sediment geochemistry, anoxic below sea surface without tidal influence, SO ₄ reducing bacteria present

The Hawaii Undersea Military Munitions Assessment (HUMMA) documented the current condition of conventional and chemical munitions that were sea-disposed between 1920 and 1951 at Sea Disposal Site Hawaii Number 5 (HI-05). Extensive digital image and video reconnaissance logs were used to classify the integrity of 1,842 UWMM (Silva and Chock 2016). The majority (66%) of the munitions were observed to be significantly corroded, but visually intact on the seafloor, and 29% were severely corroded and breached, and their contents were exposed. Unusual corrosion features such as secondary concretions were described but not fully investigated because actual samples were not collected. Similarly, chemical munitions in the

Bornholm Basin, Baltic Sea, were reported as “completely corroded” by Sanderson and Fauser (2015), and in the Adriatic Sea, the corrosion was reported as extensive enough that chemical agents were spread on the surrounding sediment surface (Amato et al. 2006).

Contrasting to the aforementioned studies that focused primarily on the corrosion conditions of chemical munitions, relatively less is known about the corrosion status of conventional munitions. A technology demonstration effort at Sea Disposal Site HI-06 (“Ordnance Reef”) was conducted in 2011 to recover and demilitarize the DMM by degrading explosives and propellants using the energetic hazard demilitarization system, and to recycle the empty DMM casings (Carton et al. 2012). Ordnance Reef is a shallow-area fringing reef approximately 8 km² in size adjacent to the Waianae shoreline on Oahu, Hawaii that was used as a disposal field for DMM after World War II. It is estimated that approximately 20 different types of munitions and over 2,000 individual rounds are present at Ordnance Reef (Garcia et al. 2009). Some of the DMM specimens that have been under water for more than 60 years were characterized for their actual corrosion morphology. An iron hydroxylchloride was identified as the primary phase together with Fe₃O₄ (iron (II,III) oxide) and β -FeOOH (akaganéite) in the inner rust layer on the projectile. A thick concretion layer consisting of an inner black FeCO₃ (ferrous carbonate) layer and an outer grayish-white CaCO₃ layer formed outside of the iron hydroxylchloride layer. Iron sulphide was also detected in the black concretion layer, indicating the effect of sulphate-reducing bacteria (Li et al. 2016). Authigenic mineral precipitation and biological overgrowth may slow corrosion rates due to the protective role of marine concretion (MacLeod 2016). Corrosion also appears to be inhibited when munitions are buried in sediments or exposed to anoxic conditions (Wang et al. 2011; George et al. 2015; Srinivasan and Hihara 2016).

3.2 Tracing the Fate of the Energetics Released in Temperate Marine Ecosystems

A series of aquarium and large mesocosm scale experiments were conducted using stable isotope labeled TNT and RDX (Figure 3-2) (Ariyaratna et al. 2019, 2020; Ballentine 2016, Smith et al. 2013, 2015a, 2015b; Tobias 2019). Experiments simulated shallow temperate coastal environments and focused on the competing fates of biotic uptake and storage versus mineralization (i.e., formation of inorganic constituents that are assumed as non-toxic or bioaccumulative) for these MC. These processes were examined under conditions that simulated three typical coastal ecotypes: subtidal low carbon sand, subtidal higher organic carbon vegetated silt, and intertidal salt marsh. The majority of experiments were conducted with a constant flow-through delivery of labeled compound, to simulate the slow leaching of either degraded UWMM or input from groundwater or surface runoff at the coast. The guiding principle for using the stable isotope tracer was that the parent compound, quantifiable organic derivatives as well as unknown transformation derivatives (calculated by difference), and inorganic mineralization products were tracked. Parent compound and organic derivatives

moving through the sediments and biota along with the isotope tracer would indicate uptake storage and retention with little processing. A divergence between the amount of tracer accounted for by the parent compound plus derivatives and the amount of tracer found in bulk sediments, biota, and mineralization products would indicate extensive breakdown and formation of non-solvent-extractable conjugates and/or mineralization.

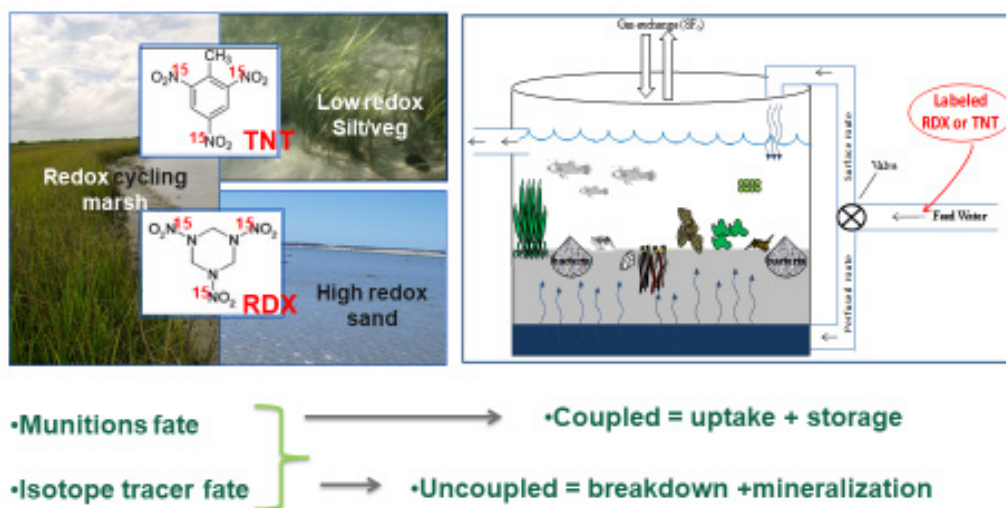


Figure 3-2. Design of the MC ^{15}N isotope tracer experiments. Either ^{15}N -labeled TNT or RDX (nitro group labeling) was used in a particular simulated ecotype. MC concentrations and ^{15}N concentrations were measured in multiple biotic and abiotic components of the ecosystem. Coupled movement of tracer and MC indicated MC uptake and storage (i.e., persistence). Divergence between MC and tracer indicated MC processing and mineralization.

In the experiments, following addition of labeled compound, the water column, sediments, and biota were analyzed for the parent compounds, primary organic derivatives, and nitrogen containing mineralization products that included ammonium, nitrate, nitrous oxide, and dinitrogen gas. Geochemical parameters of sediment and water column were also measured to correlate mineralization or retention with environmental factors.

Initial aquarium-scale static pulse addition experiments with no biota were conducted to document the behavior of TNT and RDX in simulated marine systems containing water and sediments collected from Long Island Sound, CT. The addition of sediments and sediment grain-size had a major influence on the removal kinetics of all compounds detected (Figure 3-3). Photodegradation had a negligible influence on fate for both MC due to the high light attenuation typical of temperate coastal systems (i.e., unlike clear tropical waters). RDX was stable in the absence of sediment. Sediment increases loss of both compounds from overlying water. Fine-

grained sediment was more effective than coarse-grained in removing MC from the water column. RDX degraded only in the presence of sediment, and TNT degraded significantly faster in the presence of sediment. Both compounds were removed from the system faster with decreasing grain-size. Based on these findings and a thorough review of the literature, it became evident that TNT removal rates in coastal marine waters are controlled by sorption and rapid surface-mediated bacterial transformation, while RDX removal rates are controlled by diffusion into sedimentary anoxic regions and subsequent anaerobic bacterial mineralization. A comparison of removal rates of RDX and TNT highlights the extreme variability in measured degradation rates and identifies physicochemical variables that co-vary with the breakdown of these munitions compounds (Smith et al. 2013).

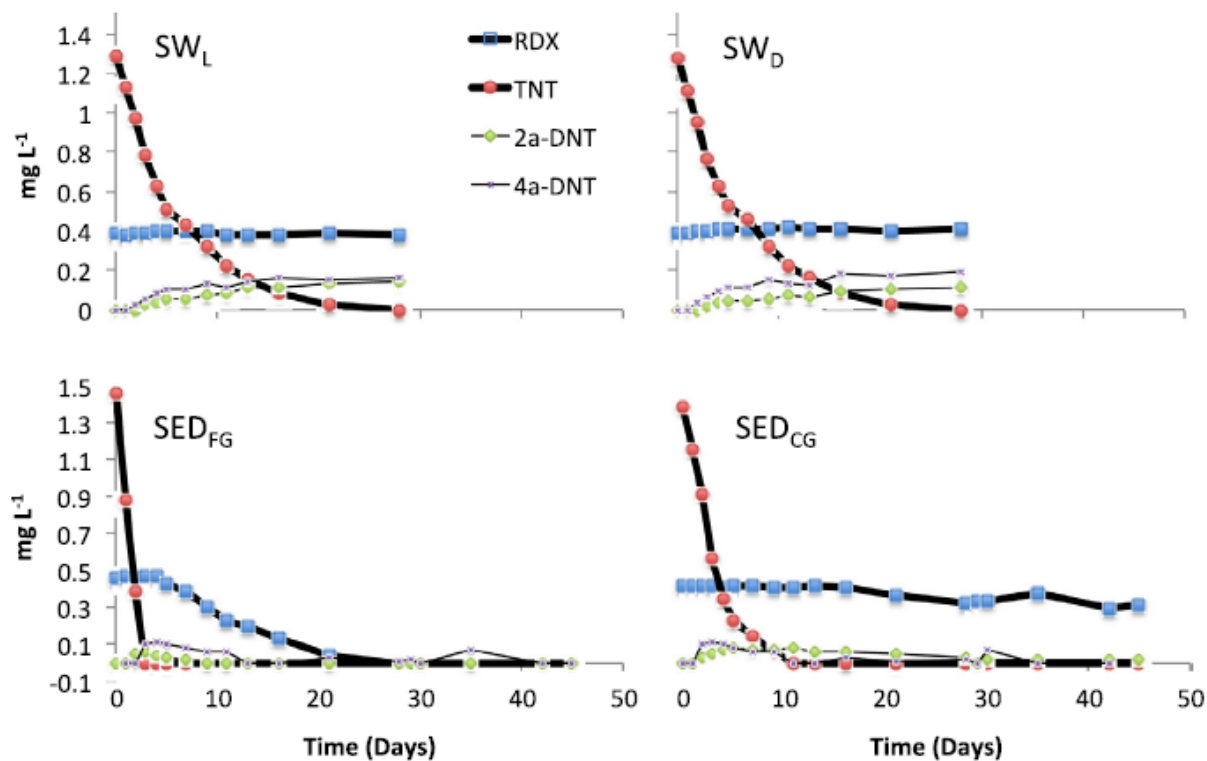


Figure 3-3. Time series concentrations of TNT, RDX, and detected organic derivatives in the four aquaria. Seawater only - light (SW_L) and Seawater only - dark (SW_D) treatments were both carried out under the same conditions with no sediment and are shown as evidence of repeatability of the experiment. Seawater + fine-grained sediment (SED_{FG}) and seawater + coarse-grained sediment (SED_{CG}) treatments were carried out with the same water type (Long Island Sound coastal water) but with fine- and coarse-grained sediment from Long Island Sound, respectively. Concentrations along the y axis are in $mg\ L^{-1}$.

A separate series of experiments were conducted in large (1,000 L) flow-through mesocosms addressing three coastal ecotypes, namely sand, vegetated silt, and intertidal salt marsh. Both TNT and RDX were 'lost' from aqueous phase, more so for TNT in all habitat types. Losses were dominantly mediated by sediments especially for RDX. Losses of RDX depended on habitat type, TNT losses did not (Figure 3-4). The measured inputs and outflow of RDX and TNT in each experiment was used to calculate a predicted aqueous concentration assuming no reactive losses. For all three ecotypes, RDX aqueous concentrations decreased from starting concentrations. The resulting steady state concentrations of both TNT and RDX were less than that predicted by conservative mixing. TNT loss was accompanied by production of ADNT derivatives. No RDX nitroso-derivatives were detected in the water column (Figure 3-4).

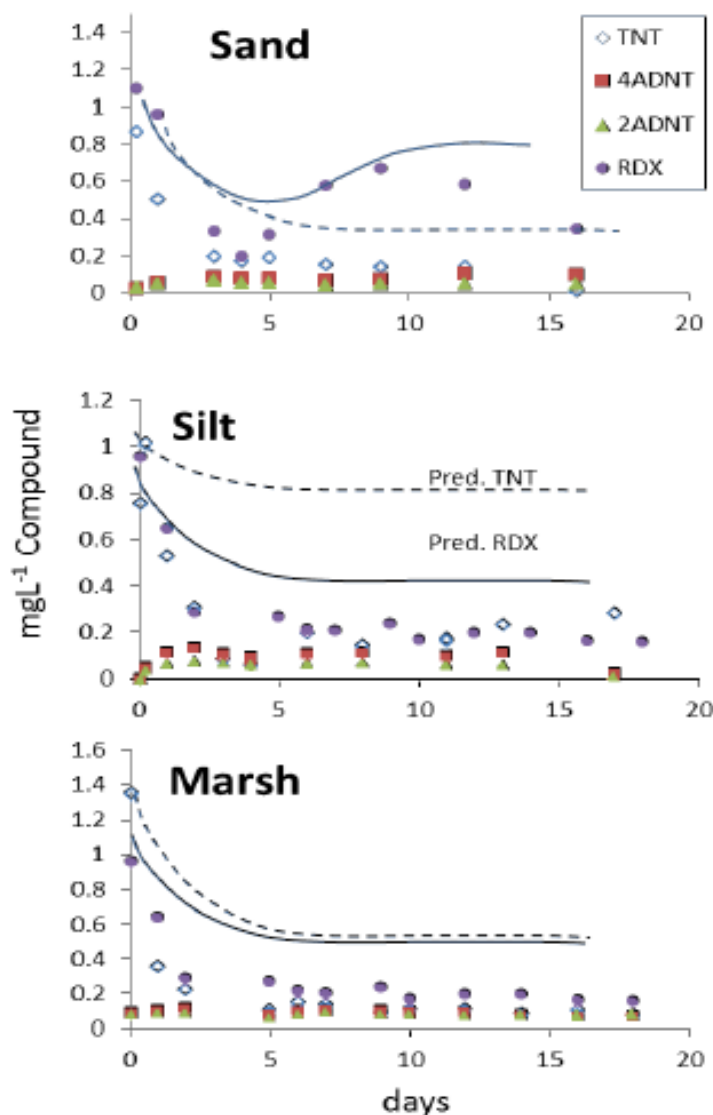


Figure 3-4. Time series parent MC concentrations in flow-through mesocosm experiments where an initial pulse of MC was followed by continued delivery of MC to achieve a steady state supply. Conservative MC behavior is predicted by the solid and dashed lines. The upward inflection in RDX in the sand mesocosm reflects temporary failure of the metering pump delivering RDX.

Both RDX and TNT and their primary derivatives are not readily taken up and stored by biota. ¹⁵N tracer in biota can account for only a few percent of the amount of parent compound removed from the water column. Marine organisms have low bioaccumulation factors (BCFs) for both TNT and RDX (Ballentine et al. 2015). Tissue concentrations of Σ TNT (TNT + 4-ADNT + 2-ADNT) and Σ RDX (RDX + hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine [MNX] + hexahydro-1,3,5-trinitroso-1,3,5-triazine [TNX] + hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazin [DNX]) in flora and

fauna are small and account for, on average, less than 10% of the ^{15}N tracer found in biota. On one hand these low tissue concentrations suggest that the ecological risks of TNT and RDX are likely to be small at aqueous concentrations in the range of our studies ($\leq 1\text{ppm}$). However, the accumulation of the isotope tracer in excess of tissue ΣTNT and ΣRDX levels indicate that breakdown within organisms is followed by retention of some of those breakdown products. It is unknown if those products that are retained represent an additional toxicological risk or not.

Sediments were a larger sink for TNT than for RDX by a factor of four. The ^{15}N tracer in sediments accounted for 5-19% vs 1-5% of TNT and RDX removed from the overlying water respectively. For both compounds, the parent compounds and primary derivatives accounted for only a few % of the isotope tracer inventory found in sediments and associated with suspended particulate matter (SPM). Sediments were sites for active transformations of both RDX and TNT the results of those transformations differ for RDX and TNT. It has long been thought that reduction of the nitro groups in TNT can lead to the production of 2,4,6-triaminotoluene (TAT) which is covalently bonded to sediments. This mechanism incompletely explains our tracer observations. The total ^{15}N in sediments approximates steady state over time which suggests the presence of other sinks in addition to transformation to products that will covalently bind to sediment. Further, the isotope mass balance in TNT experiments was poor and pointed to unmeasured and unknown organic derivative(s) as the principal fate of TNT in all coastal ecotypes (Figure 3-5). Principal component analysis results suggested the likelihood that this missing derivative(s), occurred in the aqueous phase although its formation was associated with sediments or SPM. Isotopic investigations of the bulk dissolved organic nitrogen fractions provided some confirmation that a minimum of 15 to 55% of the missing tracer in the mass balance was in the form of an organic derivative in the water column. Beyond that, the identity of the missing derivative(s) remains unknown. Complete mineralization of TNT (almost solely to NH_4^+) was a minor route of TNT processing. The primary fate of TNT in shallow coastal marine systems appears to be that of transforming into organic derivatives that may be relatively persistent in both the sediments and water column. The toxicity associated with the measured amino-dinitrotoluenes has been assessed (Lotufo et al. 2017), but the toxicological significance of the “missing” derivative(s) remains unknown until those compound(s) can be identified.

The fate of RDX was considerably different than that of TNT. RDX mineralization to dissolved inorganic nitrogen products accounted for approximately half of the RDX delivered to coastal ecosystems. In the presence of high organic and/or variable redox sediments, mineralization was the dominant fate of RDX. The nitroso-derivatives do not substantially accumulate in sediments or overlying water and instead appear to be transient intermediate species on the path to complete mineralization. Based on isotope mass balance, uncharacterized organic derivatives (those other than TNX, DNX, and MNX) are the likely the fate of less than 20% of RDX inputs. Nitrous oxide and N_2 gas were the primary terminal mineralization products for RDX, the latter

of which is reliant on naturally occurring denitrifying populations to reduce N_2O to N_2 (Figure 3-6).

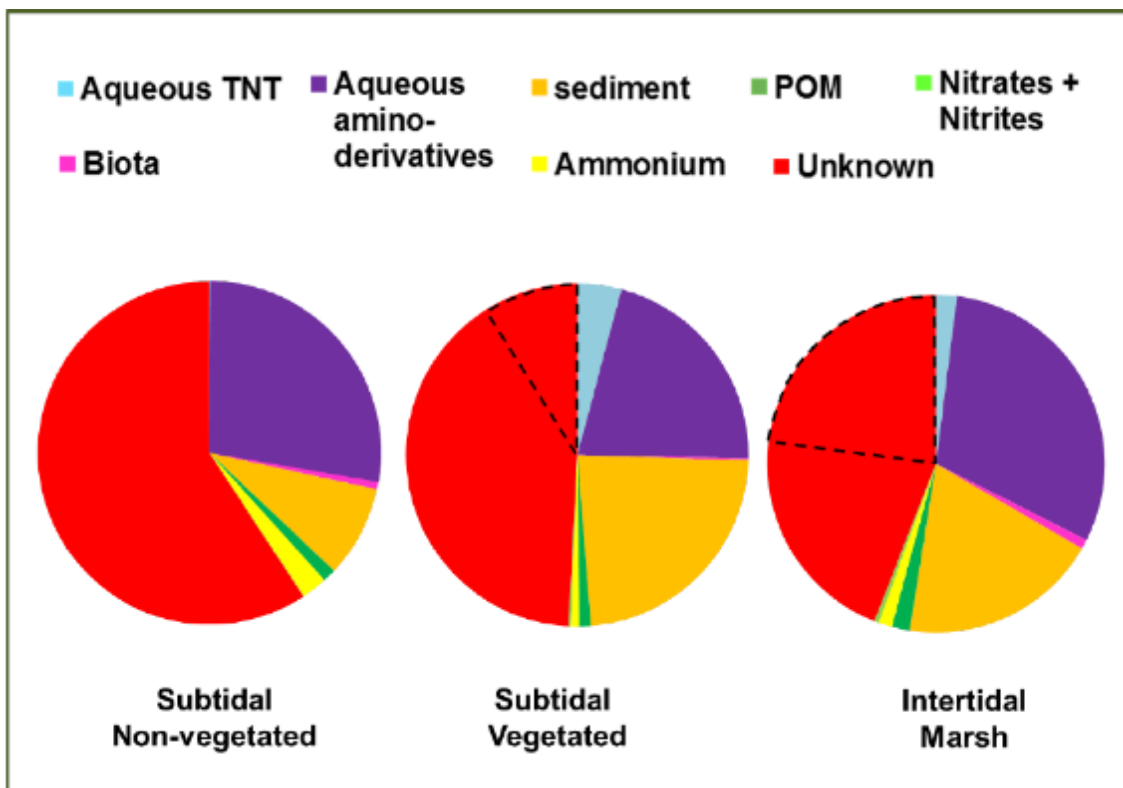


Figure 3-5. Cumulative distribution of isotope tracer in TNT mesocosm experiments. Mass balance is dominated by an unknown and presumed unmeasured organic derivative. The dashed section of the 'unknown' wedge denotes the minimum amount of that fraction that was identified as an organic compound in the aqueous phase. It was assigned using dissolved organic nitrogen (DON) isotope analyses and calculated by difference between the ^{15}N -DON and all other measured aqueous ^{15}N pools. No DON analyses were conducted on the subtidal non-vegetated mesocosm. Mineralization is defined as the sum of the ammonium and nitrate/nitrite fractions. Only trace amounts of labeled N_2 and N_2O were measured.

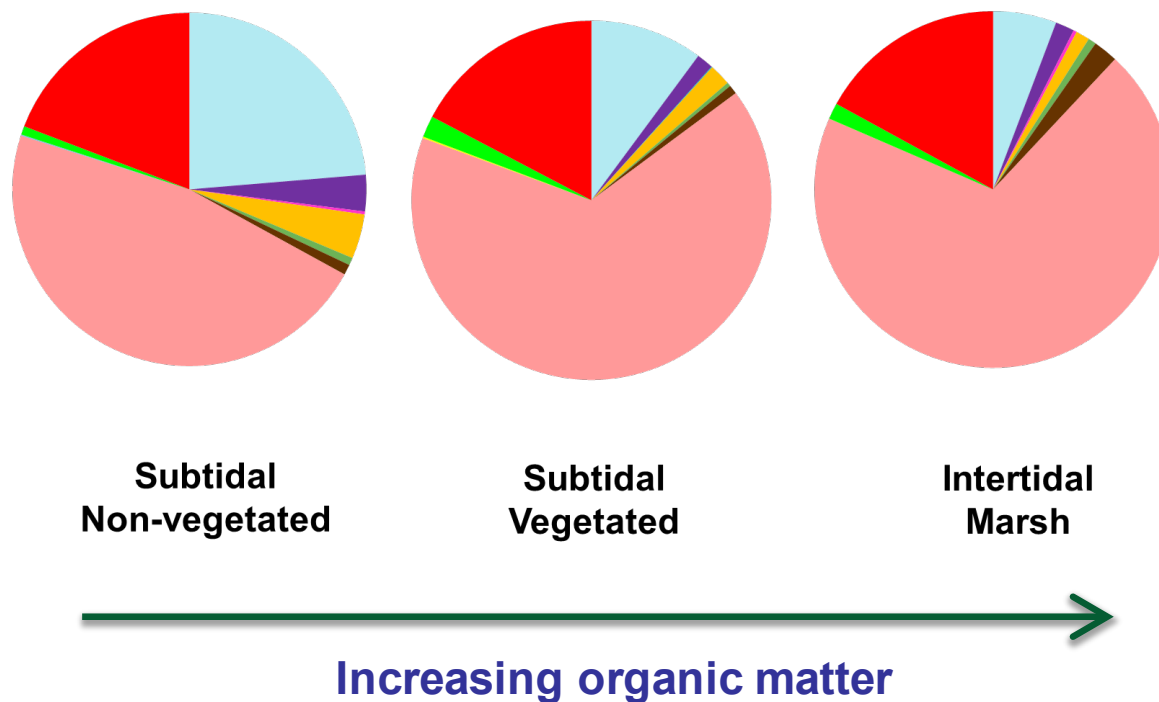


Figure 3-6. Cumulative distribution of isotope tracer in RDX mesocosm experiments. More organic matter equates with less persistence of RDX and derivatives. Mineralization is defined as the sum of the N_2 , N_2O , ammonium, and nitrate/nitrite fractions.

Results from all RDX and TNT ^{15}N isotope tracer experiments are compiled in the final report for [SERDP Project ER-2122](#) (Tobias 2019).

3.3 Sampling Water, Sediment and Biota

After resting for 70 years or longer on the seabed or other at the bottom of other aquatic environments, UWMM have the potential to corrode, breach, and release (“leak”) MC into the surrounding environment (Maser and Strehse 2020). As a result of slow release from corroding UWMM and rapid removal of MC in the surrounding water, MC is expected to be present at UWMM sites mainly at ultralow concentrations and with concentrations decreasing with increasing distance from the source of leaking munitions (Rodacy et al. 2001; Porter et al. 2011; Rosen et al. 2017a, 2018; Beck et al. 2019; Maser and Strehse 2020). To prevent the harmful impacts of uncontrolled explosions, controlled BIP operations are a common practice worldwide. However, *in situ* BIP methods often result in incomplete (low-order) detonation, leaving substantial quantities of the explosive material in direct exposure to the surrounding environment. Low-order BIP operations of munitions in the sea can result in the release of substantial quantities of explosive material in a wide range particle sizes which in turn result increased concentrations of TNT and its transformation products compared to concentrations

surrounding corroding but undisturbed UWMM (Strehse and Maser 2020; Maser and Strehse 2020).

Several challenges prevent accurate assessment of environmental exposure using traditional water, sediment, and tissue sampling and analyses. These challenges include a high level of effort or difficulty required to (1) identify breached UWMM that are actually releasing MC; (2) measure MC in the water column when present at low levels; (3) characterize water column exposure at the appropriate spatial and temporal scales for expressing environmental risk; and (4) measure MC in sediment and biota in spite of low sorption and bioaccumulation potentials. This section provides an overview of the sampling strategies to characterize water, sediment and biota contamination at UWMM sites. Section 3.1 summarizes the results of those studies.

3.3.1 Water Column Direct Sampling

Water sampling in the proximity of munitions at UWMM sites is detailed below for studies that provided methodological information.

- Ordnance Reef study sites: Grab samples were collected by divers using Niskin bottles suspended less than 0.3 m above the sediment and adjacent to munitions (UH 2014a).
- Halifax Harbor (Canada): Grab samples were collected by divers using high-density polyethylene bottles or a hand-held device designed for the project. At specified locations in the proximity of munitions (0.3, 1, 2 and 3 m), the lids were opened to fill the bottles and then recapped (Rodacy et al. 2001).
- Point Amour (Labrador, Canada) UXO detonation site: Grab samples were collected by divers using glass bottles in proximity to munitions (Ampleman et al. 2004).
- Bahia Salina del Sur (Vieques, PR): Water samples were collected at increasing distances from a 2000-pound bomb collected in 1-liter clear plastic jars (Porter et al. 2011). Bahia Salina del Sur was selected as a demonstration site for the [ESTCP project ER-201433](#) (Rosen et al. 2017a). Divers collected grab water samples in close proximity (approximately 15 to 45 cm) to 14 unique munitions, some with visible breaches. Samples were collected by divers using 1-L amber glass bottles. At specified locations in the proximity of munitions, the lids were opened to fill the bottles and then recapped (Rosen et al. 2017a,b).
- Kolberger Heide, Southwest Baltic Sea near Kiel (Germany): Water was sampled at 5, 10, 20, 40, and 60 cm from the surface of a piece of exposed munition piece using polypropylene syringes filled by divers (Beck et al. 2019).
- Shipwrecks south of Halifax, Canada: A remotely operated vehicle (ROV) took samples using glass bottles that captured water at desired locations using a trigger mechanism (Ampleman et al. 2004).
- Sea Disposal Site Hawaii 6 (HI-05) “HUMMA study sites”: Water samples were taken by human occupied vehicle (HOV) from the randomly selected locations down-current from the

munitions, and at a height above the sediment of approximately 1 to 1.5 m (UH and Environet 2010).

Water sampling from the water column above, but not near munitions present in high-density were conducted at two UWMM sites as detailed below.

- Lakes Thun and Brienz (Switzerland): Water was sampled at various depths (up to 255 m) at Swiss lakes using Niskin-type samplers in the water column above the areas where munitions were present (Ochsenbein et al. 2008).
- Kolberger Heide: Seawater samples were collected by pumping water from different depths using a Teflon bellows pump connected to a weighted polyvinyl chloride (PVC) hose. Samples were then filtered into 1-L amber glass bottles (Gledhill et al. 2019).

3.3.2 Water Column Passive Sampling

Standard environmental sampling, such as grab sampling of surface water, only generate information for the time of sample collection. Therefore, such a sample may inadequately capture temporal changes (e.g., Poulier et al. 2015) such as changes in MC concentrations that may occur at an UWMM site, thereby providing an inaccurate measure of environmental exposure. In contrast, integrative passive sampling has been used to derive ultralow and time-weighted water concentrations for a wide range of environmental contaminants, including MC (Belden et al. 2015; Rosen et al. 2016, 2017a, 2018; Lotufo et al. 2018, 2019; Estoppey et al. 2019).

Commercially available polar organic chemical integrative samplers (POCIS) currently are the most widely used samplers for weakly hydrophobic contaminants (log octanol-water partition coefficient [K_{ow}] <3), and have recently been demonstrated as a means of improving the environmental exposure assessment of MC in laboratory-based experiments (Belden et al. 2015; Lotufo et al., 2018, 2019) as well as in the field (Rosen et al. 2016, 2017a, 2018; Estoppey et al. 2019). As POCIS are flow dependent, rendering only semi-quantitative results without flow velocity data, extensive calibration across a range of flow velocities was conducted using pure MC spiked into a 30,000-gallon flume (Lotufo et al. 2018) followed by additional validation using Composition B under different release scenarios (i.e., pin hole breach vs low-order detonation; Lotufo et al. 2019). The POCIS were also evaluated for their ability to detect low part per trillion releases in a positive control field study using a known mass of Composition B chunks deployed in an estuarine embayment similar to sites that contain UXO or DMM. The study was helpful in validating the size of the plume and the sensitivity of the samplers, with TNT and RDX concentrations becoming non-detectable more than 2 m from the source (Rosen et al. 2018). A technology user's guide for POCIS at underwater munitions sites is available to DoD end users as a result of this research (Rosen et al. 2017b).

Recent research further validating the use of POCIS for MC suggests that analysis of the polyethersulfone (PES) membrane that houses the hydrophilic lipophilic balance (HLB) sorbent is highly important, as uptake in the PES was substantial. Such uptake in the PES has been shown to delay the transfer of these compounds to the sorbent, especially for more hydrophobic MC such as TNT (Estoppey et al., 2019). Lag phases using POCIS are common in the first few days of sampling and thus results are more accurate when sampling for 7 days or more for TNT. However, care should be taken in length of deployment as compounds such as HMX will come to equilibrium during longer deployments (Belden et al. 2015). In concurrent studies with Chemcatcher and POCIS, Estoppey et al., (2019) reported that both were integrative appropriate for MC, with the former having generally lower sampling rates. They also suggest the need to correct for flow velocity, which has been pursued under [ESTCP project ER-201433](#) (Rosen et al. 2017a, Lotufo et al., 2018, 2019) using a large flume system for calibrating sampling rate under different flow rates. The use of microsensors for inexpensively monitoring flow within a POCIS canister was explored at a proof-of-concept level in [SERDP project ER-2542](#) as well as using nylon screens to reduce the impact of flow at the surface of the POCIS (Belden et al. 2016). The USEPA's Office of Research and Development (ORD) and Regions 2 and 10 have a study underway examining the feasibility of performing equilibrium passive sampling for munition chemicals in both water column and sediment deployments (Rakowska et al. 2019).

Ethylene-vinyl acetate (EVA) passive samplers also show promise for quantifying MC in the water column (Warren et al., 2018). The potential advantages of EVA are that the target compounds come directly into contact with the thermoplastic material that has both hydrophobic and hydrophilic components, eliminating the need for a membrane, and therefore, potential flow or other related artifacts for uptake. The percent acetate polymer in the sampler can also be manipulated to target specific chemical type.

3.3.3 Sediment Sampling

Sediment sampling at UWMM sites is detailed below for studies that provided methodological information.

- Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA): surface and subsurface samples were collected from 43 locations without regard to proximity to buried munitions. Surface samples were collected from a research vessel using a 0.1 m² stainless steel Van Veen grab. Subsurface samples were obtained by coring (NAVFAC NW 2010a; Pascoe et al. 2010).
- Ordnance Reef (HI): Divers collected sediment samples by scooping sediment from the top 2 to 4 cm of the substrate directly into pre-labeled gallon-sized plastic storage bags. When possible, given bottom conditions and the presence of an adequate amount of sediment for

analyses, samples were collected directly adjacent to, and approximately 1 m and 2 m away from specific munitions (UH 2014a, b).

- Halifax Harbor: Samples were collected by divers by manually filling amber, high-density polyethylene bottles with seabed material collected 0.3, 1.0, 2.0, and 3.0 m from the target UWMM. The seabed was often rocky, so sediment samples were not always available (Rodacy et al. 2001).
- Point Amour (Labrador, Canada) UXO detonation site: Samples were taken by divers using unspecified sampling containers in proximity to munitions (Ampleman et al 2004).
- Former Seattle Harbor piers 90 and 91 (WA): Thirteen sediment samples were collected, eight of which were collected under munitions items located on the surface of the seafloor. Three samples were collected below excavated (removed) munitions items. Sediment samples were collected with a hand-held coring device deployed by divers (USACE 2013).
- Bahia Salina del Sur (Vieques, PR): Sediment samples were collected using a Nalgene pipette and placed in a 1-liter wide mouth, clear plastic sample container at increasing distances (adjacent, and 1, 2 and 15 m) from a 2000-pound bomb (Porter et al. 2011).
- Bahia Salina del Sur (Vieques, PR): For [ESTCP project ER-201433](#), divers collected surface sediment samples using 5-inch cores at four locations, three in close proximity to munitions (at two distances, ~ 0.5 m and 1 to 2 m from munition. At the same locations, divers also took sixteen 60-mL syringes full of porewater collected using PushPoint samplers that yielded approximately 1 L of porewater from each sampling location (Rosen et al. 2017a).
- Shipwrecks south of Halifax, Canada: An ROV took sediment samples by coring using aluminum tubes (Ampleman et al. 2004).
- HUMMA study sites (HI): Sediment samples were taken by HOV. For sediment sampling in 2009, six sample locations were randomly selected at each site: three at a radial distance of 3 m from the munitions object, and three at a radial distance of 6 m from the munitions object (UH and Environet 2010). During the 2012 cruise, sediments were collected at multiple distances (0, 0.5, 1.0, and 2.0 m) from each of the nine items sampled in linear transects from the nose, upper half of munitions casing, lower half of casing, and tail. Samples were collected using custom-made sediment scoops composed of PVC tubes and end caps, with a stainless steel “T”-bolt handle (Edwards et al. 2016a).

3.3.4 Sediment (Porewater) Passive Sampling

Although extensively demonstrated and validated for hydrophobic contaminants (Burgess et al. 2017), relatively little has been done to assess MC porewater concentrations using passive sampling. This is at least in part due to the expectation that most conventional MC of interest have relatively little affinity for sediment, and munitions items munitions proud of the bottom are likely to leak into the water column or epibenthic environment. For [ESTCP project ER-201433](#), Henry samplers attached to syringes were used to extract porewater *in situ* adjacent to ordnance at Bahia Salina del Sur (Vieques, PR) due to the desire to collect these samples in one trip to the

site (Rosen et al. 2017a). As part of a SERDP Exploratory Development (SEED) Project (Edmitson (2017); [SERDP Project ER-2541](#)), thiolated organosilica sorbents (i.e Osorb®) were evaluated for measuring the bioaccessible fraction of TNT and RDX in spiked sediments. As noted above, the USEPA's ORD and Regions 2 and 10 have a study underway examining the feasibility of performing equilibrium passive sampling for munition chemicals in both water column and sediment deployments.

3.3.5 Biota Sampling

Biota sampling at UWMM sites is detailed below.

- Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA) (NAVFAC NW 2010b): Six individual Starry flounder (*Platichthys stellatus*) were collected by hook and line method from a sampling vessel. Graceful crabs (*Cancer gracilis*) were collected using crab pots deployed and retrieved from a sampling vessel. Clams (*Macoma nasuta*) were collected during low tide periods. Six individual sea cucumber (*Parastichopus californicus*) samples were collected in shallow water by divers.
- Ordnance Reef study sites (UH 2014a,b): Target biota species were selected based on discussions with local community members. Octopi (*Octopus cyanea*) were caught using a tactical spearing technique, Kona crab (*Ranina ranina*) were caught in bottom traps, and seaweed (*Asparagopsis taxiformis*) was harvested by hand. Fish (red wake and white wake; *Mulloidichthys flavolineatus* and *M. vanicolensis*) were trapped in nets left in place overnight at prime collection spots within each stratum. Based on a suggestion by the local community, only edible portions of the biota collected were analyzed.
- Bahia Salina del Sur (Vieques, PR) (Porter et al. 2011): The following biota samples were obtained near a 2000-pound bomb: a dusky damselfish, which had taken up residence inside the bomb; a feather duster worm attached to the bomb at the entrance of the corrosion hole; a mountainous star coral physically adjacent to the bomb; a grooved brain coral living 15 m from the bomb; and a long-spined sea urchin grazing on the nose-cone of the bomb.
- HUMMA study sites (Koide et al. 2016): HOVs were used to deploy and recover shrimp (*Heterocarpus ensifer*) traps at locations adjacent to the targets of interest. At each study site, the HOV placed the shrimp trap on the seafloor proximal to the main body of the DMM, within 0.5–2 m of the casing. Typically, the traps were left in place for less than two hours prior to HOV departure for another site or return to the ocean surface.
- Kolberger Heide (caged mussel studies): A mooring with two mussel bags, one at the ground directly on a bulk of explosive and one at a height of one meter, filled with 20 mussels each were placed at a depth of approximately 11 m in close proximity to blast craters with explosive material (hexanite) scattered in the vicinity as a result of selective blasting. The exposure period was 93 days (Strehse et al. 2017). In a related study, Appel et al. (2018) and Maser and Strehse (2020) deployed caged mussels at Kolberger Heide near areas high-density of moored mines discarded after World War II as well as in areas where pieces of explosive material (5–30 cm in diameter) resulting from BIP events were scattered on the seafloor.

Mussels were also placed in areas where no pieces of explosive material were lying on the seafloor. Exposures were 106 and 146 days long. Maser and Strehse (2020) and Strehse and Maser (2020) provide an overview of the results of all mussel monitoring studies at Kolberger Heide.

- Kolberger Heide (resident biota study): In a preliminary study at the site, algae, tunicates and starfish were sampled manually by divers within close proximity of discarded mines and from a BIP crater site within 1 m of submerged munitions (Gledhill et al. 2019).
- Kolberger Heide (flatfish study): Dab (*L. limanda*) were caught and their bile was analyzed for the presence of MC in order to improve knowledge about the degree and spatial distribution of fish contamination originating from that dumpsite (Koske et al. 2020a).

3.4 Chemical Analysis of Water, Sediment and Biota Samples

Based on existing information, MC is expected to be present at UWMM sites mainly at ultralow concentrations (Lotufo et al. 2017; Beck et al. 2018), mostly because of the slow dissolution rates (Beck et al. 2018, 2019). As long as the contamination is not isolated within a limited volume of water, the high loads of water in the sea or lakes dilute the chemicals released into the environment from source (Voie and Mariussen 2018). Therefore, to adequately characterize contamination by MC in aquatic environments requires analytical methods that combines high sensitivity with unambiguous compound identification (Gledhill et al. 2019). Various methodologies have been used to measure MC in water, sediment, and biota samples at UWMM sites (see overview in Lotufo et al., 2017). This section provides an overview of analytical methods historically used to extract and quantify MC in water, sediment and biota samples collected at UWMM sites, as well as describe recently developed methods to optimize detection in complex matrices (i.e., marine biota; Craig et al. 2019) and to jointly analyze legacy and insensitive munitions compounds in environmental samples (Crouch et al. 2019). The reader should refer to Gledhill et al. (2019), Craig et al. (2019) and Rosen et al. (2017a,b) for the most up-to-date overview of analytical methods used for detection of MCs in environmental samples and for recommended methodology for use at UWMM sites in future projects. In addition, the reader should also refer to Crouch et al. (2020) for new methods of extraction, pre-concentration, and analytical separation/quantitation of legacy munition compounds along with several additional IM and IM breakdown products in water, soil and biota.

3.4.1 Water

The most widely used methodology for quantifying the concentration of MC in water samples collected from UWMM sites analysis has been solvent extraction (typically following pre-concentration by solid-phase extraction [SPE] using Oasis HLB SPE cartridges) followed by separation by high-performance liquid chromatography (HPLC), and spectrophotometric detection to achieve detection limits in the µg/L range (USEPA Methods 8330, 8330A, 8330B;

USEPA 1994, 2006, 2007a). Mobile phase conditions can result in poor peak separation and shifts in retention time, complicating compound identification using this method. Water samples collected for the Ordnance Reef (UH 2014a,b) and HUMMA investigations (Koide et al. 2016), from UWMM sites in the East Coast of Canada (Ampleman et al. 2004), and from Bahia Salinas del Sur in Vieques (Porter et al. 2011) were analyzed using USEPA method 8330.

Samples from Halifax Harbor were analyzed using solid-phase micro extraction (SPME) to sample MC in seawater near submerged munitions. SPME solvent extracts were analyzed using capillary column gas chromatography with an electron capture detector (GC/ECD) (Rodacy et al. 2001). USEPA Method 8095, a GC-ECD analytical method, has been developed with the same target analyte list as the high-performance liquid chromatography–ultraviolet (UV) detection (HPLC-UV) Method 8330A (USEPA 2007b). Ultralow detection of MC at sub-ng/L concentrations has been reported in lake water and tributaries using pre-concentration or direct injection using analytical techniques such as liquid chromatography-electrospray tandem mass spectrometry (Ochsenbein et al. 2008).

Seawater sampled in controlled field experiments (Rosen et al. 2018) and in the vicinity of UWMM at Bahia Salinas del Sur at Vieques, PR (Rosen et al. 2017a) were pre-concentrated, solvent-extracted and analyzed by gas chromatography–mass spectrometry (GC/MS) using GC methods described and optimized by Zhang et al. (2007) and USEPA method 8095 (USEPA 2007b) using negative ionization. Negative chemical ionization reduces the potential for interferences in field-collected samples. Coupling GC-MS with POCIS, low ng/L concentrations were detected in seawater.

Gledhill et al. (2019) developed a highly sensitive method for the analysis of MCs in the seawater that combines 1000-fold pre-concentration and sample clean up by SPE with separation using a polymeric styrene divinylbenzene stationary phase, and detection by ultra-high-performance liquid chromatography – electrospray ionization – mass spectrometry (UHPLC-ESI-MS) using an injection volume of 25 µL. Heavy isotopes of TNT and 1,3-dinitrobenzene (DNB) were used to improve quantification.

3.4.2 Sediment

The most commonly used methodology for quantifying the concentration of MC in sediment samples collected from UWMM sites analysis has been solvent extraction followed by USEPA Method 8330B. This method was used at site in Hawaii (Garcia et al. 2009; UH and Environet 2010; UH 2014a,b), and Canada (Ampleman et al. 2004). The USEPA developed Method 8330B to include guidance for sampling and processing of soil samples, which are also applicable to sediment. To obtain detection limits compatible with the risk evaluation used for the site, samples from Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA)

were analyzed using USEPA Method 8330B modified by the analytical laboratory specifically for that site. Different modifications were used to best suit the wide range of MC analyzed (Pascoe et al. 2010): nitroguanidine (NQ) nitrobenzene, 2-nitrotoluene (NT), 3-NT, and 4-NT by USEPA Method 8330B with HPLC-UV; picric acid, picramic acid, and 2,4-dinitrophenol by USEPA Method 8330B with HPLC-MS/MS; HMX, RDX, TNB, DNB, tetryl, TNT, 2-ADNT, 4-ADNT, 2,4-DNT, 2,6-DNT, 3,5-dinitroaniline (3,5-DNA), PETN, 2,4-DANT, and 2,6-DANT by USEPA Method 8330B with HPLC-UV and LC-MS/MS. Samples for nitrocellulose analysis were prepared following the method of MacMillan et al. (2008) and analyzed by modified USEPA Method 353.2.

The same methods were used for the analysis of samples from former Seattle Naval Supply Piers 90 and 91 (USACE 2013). Sediment samples from the studies by Rodacy et al. (2001) and Rosen et al. (2017a, 2018) were solvent-extracted in a sonicating bath and analyzed as described above for water samples.

3.4.3 Biota

Because USEPA method 8330A and method 8330B are designed for the analysis of MC in soil and water matrices, modifications of these methods have been used for the analysis of biota sampled from UWMM sites.

For the Ordnance Reef and the HUMMA projects, all biota tissue samples (fish, crab, octopus, and seaweed) were analyzed for MC using USEPA Method 8330A modified for marine matrices (UH 2014a, 2014b; Koide et al. 2016). Modifications to method 8330A were required to resolve organic interferences and identify both a primary and a confirmation column to provide adequate resolution and response to accurately and precisely measure the concentrations of MC (UH 2014a). Reported concentrations in biota were in the double-digit $\mu\text{g}/\text{kg}$ range.

More recently, methods other than 8330A and 8330B have been used. Caged mussel samples from Kolberger Heide, a historical munitions disposal located in the Southwest Baltic Sea near Kiel (Germany), were homogenized in acetonitrile and analyzed using GC/MS (Strehse et al. 2017; Appel et al. 2018; Maser and Strehse 2020). For analytical methodology development, resident biota sampled from Kolberger Heide were analyzed (Gledhill et al. 2019). Biota samples (algae, tunicates and starfish) were frozen, lyophilized, ground and extracted in acetonitrile. Samples were sonicated, extracts filtered and diluted with ultrapure water to a ratio of 30% acetonitrile and 70% water and analyzed as describe above for water samples. The two above studies reported concentrations in biota in the single-digit $\mu\text{g}/\text{kg}$ range. Bile extracted from dab (*Limanda limanda*) was injected on a column in an Agilent 1290 Infinity High-Performance-Liquid-Chromatograph coupled to an AB Sciex QTrap 5500 Triple Quadrupole/Ion-Trap Mass Spectrometer (HPLC-MS) (Koske et al. 2020a).

Under the premise that no well-established method for the determination of MC in aquatic biota had been established, Craig et al. (2019) conducted a series of detailed experiments leading to the development of a novel method that was evaluated through a laboratory inter-comparison test. Five types of marine tissues (dungeness crab, manila clam, starry flounder, sea cucumber, and geoduck) were used. Dry-ice grinding proved successful for sample homogenization. Samples were extracted as described in Method 8330B. A cleanup procedure using SPE using Oasis HLB SPE cartridges was adequate for the removal of interferences. Sample extracts were analyzed using a reversed-phase high-performance liquid chromatography with a UV detector (RP-HPLC-UV). The Method 8330B modified for tissue analysis showed suitable detection capability, analytical accuracy, precision, sensitivity, linear range, and robustness for all analytes investigated, except for tetraol, for all five tested marine tissue matrices.

3.5 Toxicity of MC to Aquatic Biota

To support the assessment of risk associated with the presence of MC in aquatic environments, contaminant-spiked water or sediment are often used in laboratory experiments to derive toxicity data for a variety of freshwater and marine species and endpoints. In order to bracket the toxic range and derive toxicity benchmarks, most studies involve the use of exposure concentrations significantly higher than those expected in the environment. Talmage et al. (1999) provided a broad overview of the effects of explosive compounds to aquatic organisms and Nipper et al. (2009) compiled available aquatic toxicity data, which was expanded to include nitroaromatic and nitrophenolic compounds that are not energetic compounds or their transformation products. Lotufo et al. (2009b) reviewed the available sediment toxicity data. Additional comprehensive overviews of the toxicity of MC to aquatic biota are available (Lotufo et al. 2013, 2017).

The broad summary on the toxicity of MC to aquatic biota derived from water-only and sediment toxicity tests provided in this section is based on recent data compilations and detailed overviews by Lotufo et al. (2013, 2017). The reader is encouraged to refer to Lotufo et al. (2017), a more detailed overview that provides access to a database containing the available toxicity information and associated references. Lotufo et al. (2017) also summarizes information on biochemical and histopathological effects of MC in aquatic biota, which are not summarized in this section. Brief summaries of recent studies not included in Lotufo et al. (2013, 2017) are provided at the end of this section.

3.5.1 Toxicity to Aquatic Autotrophs

TNT caused decreased population growth of cyanobacteria and green microalgae, at concentrations ranging from 0.75 to 18 mg/L. Overall, mono-amino transformation products of

TNT exhibited lower toxicity to microalgae compared to the parent compound. The nitroaromatic compounds 2,4-DNT and 2,6-DNT caused decreased population growth of microalgae at a range (0.9 to 16.5 mg/L) similar to that reported for TNT. Nitroaromatics impacted sea lettuce zoospore germination at concentrations ranging from 0.05 to 4.4 mg/L, with TNB being the most toxic compound tested, followed by TNT, 2,4-DNT, and 2,6-DNT. Cyanobacteria and algae were relatively tolerant to the effects of RDX, with effects on population growth reported at 12.0 to 36.7 mg/L. Exposure to HMX at reported concentrations that approached or exceeded its solubility limit failed to decrease population growth of cyanobacteria and microalgae. Aquatic autotrophs were relatively tolerant to picric acid, but sensitive to tetryl, with sublethal effects reported at 61 mg/L and higher concentrations and 0.43 mg/L, respectively. Exposure of freshwater microalgae to NG resulted in decreased population growth and reduction in chlorophyll *a* at concentrations as low as 0.4 mg/L. Exposure to diethylene glycol dinitrate (DEGDN) caused decreased population growth of a microalga at 58 mg/L and NQ caused decreased population growth and reduction in chlorophyll at 508 mg/L or higher concentrations.

3.5.2 Toxicity to Aquatic Invertebrates

Numerous aquatic toxicity studies have reported that TNT, its aminated transformation products or the related compounds TNB, 2,4-DNT and 2,6-DNT caused decreased survival to freshwater and marine and estuarine invertebrates. The toxicity of MC to corals is detailed in section 2.6 of this report. Toxicity to most species occurred within the range of 1 to 6 mg/L. A decrease in offspring production at concentrations lower than those promoting mortality was reported for a cladoceran exposed to 2,4-DANT, a cladoceran and a rotifer exposed to TNT, and a polychaete exposed to TNT, TNB, 2,4-DNT, or 2,6-DNT.

For some aquatic invertebrate species, both marine and freshwater, RDX was not toxic even at the maximum concentration tested. For example, exposure to RDX at 7.2 mg/L failed to elicit mortality of coral and exposure to RDX concentrations approaching its solubility limit in water (28 mg/L or higher concentrations) failed to elicit significant mortality in marine invertebrates. However, RDX caused mortality or decreased reproduction at sublethal concentrations in some freshwater and marine invertebrate species. All freshwater and marine invertebrate species investigated were unaffected by the highest concentrations of HMX tested, even at the solubility limit for that explosive.

When comparing the toxicity of eight explosives and related compounds to marine invertebrates, tetryl was the most toxic compound overall, with toxicity occurring at 1 mg/L or lower concentrations. Picric acid was lethally toxic at much higher concentrations to freshwater and marine invertebrates, as lethal levels ranged from 13 to 379 mg/L for a variety of marine invertebrates. Picric acid promoted a significant decrease in sea urchin embryonic development

and copepod hatching success at concentrations lower than their respective lethal concentrations.

For freshwater invertebrates, lethal effects of NG exposure occurred at 17 to 18 mg/L, and lethal effects of DEGDN occurred at 90 to 491 mg/L. For a copepod and a cladoceran, the single species of aquatic organism investigated for the toxicity of PETN, no lethal or sublethal effects were observed at the highest concentration tested, 32 mg/L and 49 mg/L, respectively. Aquatic invertebrates were relatively tolerant to exposure to NQ, with toxicity occurring at 440 mg/L or higher concentrations. Studies with nitrocellulose indicated no toxicity to freshwater invertebrates at concentrations up to 1,000 mg/L. The overall lack of toxicity of nitrocellulose is likely a result of its insolubility in water.

3.5.3 Toxicity to Tadpoles and Fish

TNT, its aminated transformation products or the related compounds TNB, 2,4-DNT and 2,6-DNT caused decreased survival to larval freshwater, marine and estuarine fish from 0.4 to 28 mg/L. The TNT transformation product 2,4-DANT was not toxic at the highest concentration tested (50 mg/L). Survival of tadpoles was significantly decreased at concentrations as low as 0.003 mg/L for TNT and 0.13 and 0.21 mg/L for 2,4-DNT and 2,6-DNT, respectively during chronic exposures (i.e., 28 or 90 d), suggesting that larval amphibians may be much more sensitive than fish to the long-term effects of nitroaromatic explosives.

The nitramine, RDX, caused lethal or sublethal impacts to freshwater and estuarine fish at concentrations ranging from 2 to 28 mg/L. Studies with freshwater fish demonstrated that larval fathead minnows were susceptible to the effects of HMX at exposure solutions saturated with HMX. Except for the report of toxicity to fathead minnows, all other species of freshwater and estuarine fish investigated were unaffected by the highest concentrations of HMX tested. The highest no-effect concentration reported in those studies were higher than the reported aqueous solubility limit of HMX.

When the toxicity of eight explosives and related compounds to embryos of a marine fish was compared, tetryl was the most toxic compound overall, with toxicity occurring at 1 mg/L. It was also the most degradable compound, often being reduced to very low or below-detection levels at the end of the test exposure. In contrast to the high toxicity of tetryl, the nitrophenolic explosive picric acid was lethally toxic to fish at much higher concentrations. Lethal effects to freshwater fish exposed to NG occurred at 1.9 and 3.6 mg/L. For DEGDN, lethal effects to fish occurred from 258 to 491 mg/L. Fish were tolerant to exposure to NQ, with no significant lethality occurring at exposure concentrations exceeding 1,500 mg/L.

3.5.4 Toxicity of Spiked Sediment to Aquatic Invertebrates and Fish

Rapid transformation, disappearance of transformation products, and partitioning to overlying water following initiation of whole sediment toxicity testing has been reported for TNT and its amino transformation products, and for TNB, 2,6-DNT, picric acid and tetryl. The rapidly changing concentration of explosives and their transformation products in exposures to sediment presents unique challenges to the process of developing accurate toxicity data for the evaluation of risks to biota at contaminated sediment sites. Ideally, toxicity evaluations of nitroaromatic explosives-spiked sediments should use exposure conditions (e.g., duration, water quality requirements) that minimize degradation of the parent compound and that do not require water changes during the experimental period.

Compared to investigations addressing explosives and related compounds in soil exposures, relatively few studies addressed the toxicity of sediment-associated explosives to freshwater and marine invertebrates and to fish in exposures to spiked sediments. The toxicity of sediment amended with TNT to marine polychaete, estuarine amphipod, freshwater midge, amphipod, oligochaete and estuarine fish occurred within a wide range of concentrations (37 to 508 mg/kg). The observed variability in the effects concentrations was due at least in part to challenges associated with accurately characterizing the exposure concentrations. The toxicity of transformation products of TNT-spiked to sediments evaluated for marine and estuarine and freshwater invertebrates revealed that although the species investigated varied widely in responsiveness, TNT, 2-ADNT and TNB caused toxicity at relatively similar concentrations to each species. The toxicity of sediments spiked with 2,6-DNT was examined using a marine amphipod. No lethal toxicity was observed in any treatment and because the highest 2,6-DNT measured concentration in sediments was relatively low (5 mg/kg), the effects of that compound at higher concentrations remain unknown.

The toxicity of sediments spiked with RDX and HMX was reported for a polychaete and two marine amphipod species, and for a freshwater midge and an amphipod species. No significant mortality was observed in sediment concentrations of RDX ranging from 102 to over 2,000 mg/kg, and HMX concentrations ranging from 115 to 353 mg/kg, suggesting high tolerance of benthic invertebrates to these explosives. The toxicity of picric acid and tetryl spiked to sediments was examined using a marine amphipod. Significant lethal effects in exposures to spiked sandy sediment were observed at picric acid concentrations similar to lethal concentrations reported for marine amphipods exposed to TNT, but tetryl resulted in significant lethal effects at concentrations as low as 4 mg/kg.

3.5.5 Summary of Recent Studies

Recent data compilations and detailed overviews on the toxicity of MC to aquatic organisms are available (Lotufo et al. 2013, 2017). For completeness, recent studies not included in Lotufo et al. (2013, 2017) are summarized below.

- The marine flatworm *Macrostomum lignano* was shown to stop feeding and starve when exposed to TNT at 3 mg/L, 2-ADNT at 0.33 mg/L and 4-ADNT at 0.033 mg/L (Bickmeyer et al. 2020).
- Koske et al. (2019) recently proofed deoxyribonucleic acid (DNA) damaging effects in zebrafish embryos (*Danio rerio*) from TNT and its metabolites 2-ADNT and 4-ADNT, which was the first study that demonstrated the genotoxicity of TNT on fish embryos. Lethal concentrations (LC50) were 4.5 mg/L for TNT, 13.4 mg/L for 2-ADNT and 14.4 mg/L for 4-ADNT.
- Competitive inhibition of 7-ethoxyresorufin-O-deethylase and 7-methoxyresorufin-O-deethylase by TNT *in vitro* was demonstrated for livers from three flatfish species (*L. limanda*, *Pleuronectes platessa* and *Platichthys flesus*) sampled from the Baltic Sea (Koske et al. 2020b).
- Mariussen et al. (2018) investigated the effects of TNT in juvenile Atlantic salmon (*Salmo salar*). Mortality, severe hemorrhages in the dorsal muscle tissue near the spine as well as effects on blood parameters such as of glucose, urea, hematocrit and hemoglobin occurred in fish exposed to 1 mg/L (concentration in water).
- The toxicity of dissolved NQ, DNAN and RDX to *Hyalella azteca* was investigated (Lotufo et al. 2018). DNAN was the most toxic compound, with 10-d LC50 of 16.0 mg/L; the 10-d LC50 for NQ was 891 mg/L and RDX did not elicit significant mortality up to 29.5mg/L, a concentration near its solubility limit.
- The NQ parent compound was toxic at high concentrations (e.g., 4-d LC50 = 1323 mg/L for zebrafish larvae, Gust et al. 2017; LC50 = 1,174 mg/L to *Ceriodaphnia dubia*, Kennedy et al. 2017) or not toxic at high concentrations (e.g., no lethality to larval *Pimephales promelas* at 2,640 mg/L, Gust et al. 2018) in aquatic exposures, it was found to have a marked increase in toxicity after exposure to ultraviolet light, 2-3 orders of magnitude in certain circumstances (Kennedy et al. 2017; Gust et al. 2017). It remains unknown if degradation under natural sunlight could result concentrations high enough to promote toxicity to aquatic biota (Moores et al. 2020).

3.6 **Toxicity of MC to Corals**

Coral reefs occupy less than 1% of the world's oceans, yet they form one of the most diverse ecosystems on earth, hosting an estimated 25% of all marine species. These reef systems also

deliver ecosystem services, estimated at \$30 billion, in the form of tourism, fisheries, and shoreline protection (Waddell 2005; Baird et al. 2002). The majority of coral reefs flank oceanic islands throughout tropical and subtropical oceans between 30°S and 30°N latitude. Because most reef-building coral have narrow physiological tolerances and are photosynthetic, they are predominantly found in oligotrophic waters at depths less than 30 meters with sufficient light penetration (Waddell 2005).

Over 20 U.S. military base installations are adjacent to coral reef environments in the Caribbean (e.g., Key West, FL, Puerto Rico, Guantanamo, Cuba) and Pacific Islands (e.g., Hawaii, Republic of the Marshall Islands, American Samoa, Guam, Okinawa, Japan, Philippines, Mariana Islands). In addition to military bases, DoD has numerous training areas, particularly in the Pacific, where munitions and UXO can be found in shallow coral reef environments (e.g., Vieques, Puerto Rico; Ordnance Reef, Ohau HI; Kahoolawe HI; Camel Rock in Asan Bay Guam; Island of Farallon de Medinilla, Mariana Islands; Kwajalein Atoll, Johnson Atoll, Midway).

Coral reefs clearly co-occur with many military bases and training areas throughout the Caribbean and Pacific Ocean. Range-wide, coral reefs have become at-risk ecosystems from multiple stressor impacts that include land-based sources of pollution, climate change, disease and overuse of reef resources (Wilkinson 1999; Knowlton 2001; Pandolfi et al. 2003, 2005; Ramade and Roche 2006; Reopanichkul et al. 2009). Over the last several decades, there has been heightened recognition that coral reefs worldwide are failing. In 2006, two Caribbean species were listed as ‘threatened’ under the Endangered Species Act (ESA) and in October 2014, 20 additional coral species (5 Caribbean and 15 Indo-Pacific) were listed as threatened under ESA (NMFS 2014). Thus, the potential risk posed by munitions compounds to coral health and reproduction are highly relevant to DoD management decisions in balancing continuity of operations with their responsibilities for environmental compliance and stewardship.

This section summarizes Woodley and Downs (2014, [SERDP Project ER-2125](#)) and provides an evaluation of the toxicity of MC to corals and provides screening values for levels of concern (LOC) and potential action values to support management decisions.

3.6.1 Methods

Coral Culture

Pocillopora damicornis, a Pacific branching coral, was the primary species used in these studies. Specific experiments used laboratory reared adult coral fragments, coral primary cell cultures, and coral algal symbiotic cell cultures isolated from *P. damicornis*. *Porites divaricata* (Caribbean branching coral) and *Porites lobata* (Indo-Pacific mounding coral) primary cell cultures were used in limited experiments for species sensitivity comparison.

Corals were grown in glass/Teflon® multi-tank systems (e.g., Figure 3-7 and 3-8) and dosing systems were similarly constructed at both Haereticus Environmental Lab (HEL) and at the NOAA NOS Charleston SC, Coral Culture Facility. The use of glass and Teflon was considered a critical element of our toxicological studies to ensure that corals were not exposed to chronic exposures from leachates known to occur from materials commonly used in aquaculture and aquaria, such as plastics, PVC, fiberglass.

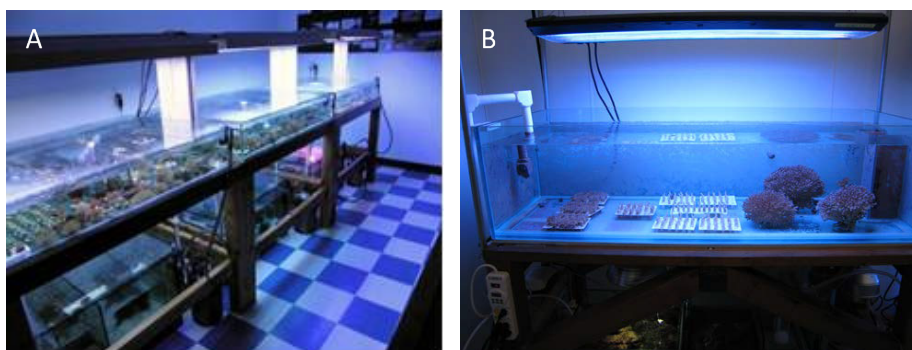


Figure 3-7. HEL glass-teflon coral culture system. A) Experimental system fabricated with all glass and Teflon® parts, the lighting system uses custom-made light-emitting diode fixtures. B) NOAA glass-teflon coral culture system. Shown are three parent *P. damicornis* colonies and fragments on custom fabricated Teflon pegs and stands.

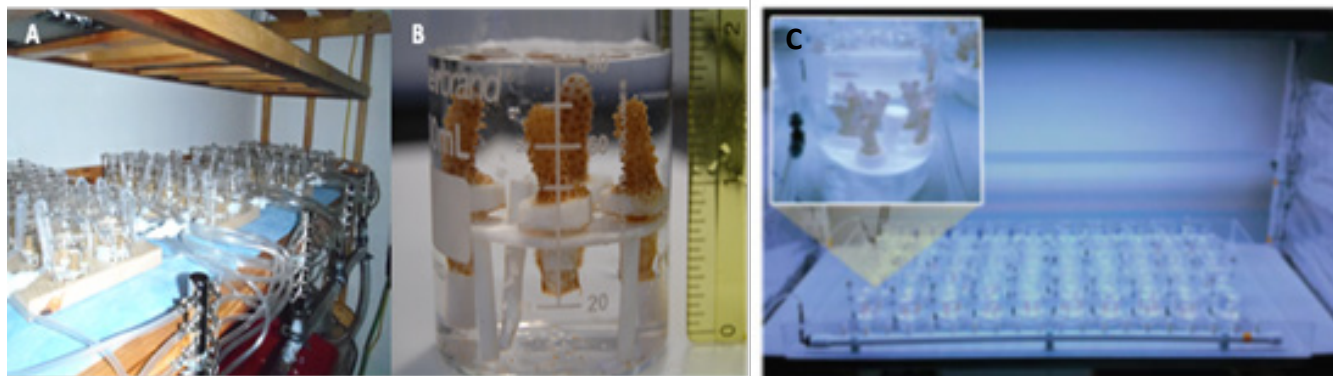


Figure 3-8. HEL and NOAA's coral fragment dosing systems. A) HEL- replicate 200 mL glass beakers fitted with individually controlled Teflon® airlines. B) HEL - close-up of individual treatment replicate. C) NOAA dosing system. Inset close-up of individual treatment replicate. Four fragments, each for separate endpoints.

Coral fragment exposures for 96 h using a static renewal (12 h) replicated design with varying treatment concentrations. Coral primary cells were exposed for 4 h in either light or dark conditions.

Munitions Compounds Tested

Stock solutions of RDX, HMX and TNT in methanol or acetone were provided by USACE Environmental Laboratory, Vicksburg, MS. Picric acid was obtained from Electron Microscopy Sciences (Hatfield, PA). Remaining compounds (3-DNT, 2,4-DNT, 2,6-DNT, 2-ADNT, 4-NT) were purchased from ChemService (West Chester, PA). Table 3-2 describes the types of testing conducted with each MC.

Table 3-2. List of munitions compounds and breakdown products tested.

MC	Specimen Tested
TNT	Coral cells Pdiv, Pdam, Pdiv frags, Dino
2,3-DNT	Pdam frags, Dino
2,4-DNT	Coral cells, Dino
2,6-DNT	Coral cells: Pdam, Pdiv, Plob, Dino
4-NT	Dino
2-ADNT	Dino
RDX	Coral cells, Pdam frags, Dino
HMX	Coral cells
Picric Acid	Coral cells
Pdam frags = <i>Pocillopora damicornis</i> coral fragments, Pdiv frags = <i>Porites divaricata</i> coral fragments, Dino = symbiotic dinoflagellate, <i>Symbiodinium</i> sp. Clade B isolated from <i>Pocillopora damicornis</i> , Plob = <i>Porites lobata</i>	

Coral Primary Cell Cultures

For coral cell model toxicity studies, *Symbiodinium* (endosymbiont)-containing gastrodermal cells and calicoblasts were prepared from *Porites lobata* and *Pocillopora damicornis* by mechanical and enzymatic disaggregation of tissue from the coral skeleton (Downs et al. 2010). Cells were distributed into treatment solutions in 24-well PTFE plates and incubated for 4 h in the light or dark conditions at 26°C. Cells were counted to determine cell mortality after exposure to MC.

Endpoints for Coral Algal Symbiont Cultured Cells

1. Cells were stained with propidium iodide (stains dead cells) and counted on a hemacytometer to determine cell population growth after exposure to MC.
2. Pulse-amplitude modulated (PAM) fluorometry was used to monitor photosynthetic activity by measuring the induction of chlorophyll *a* fluorescence from dark-adapted tissue. An Imaging-PAM was used for these measurements and produces an image that is colorized to depict the severity of effects on photosynthetic efficiency.

Endpoints for Coral Fragments

1. Visual health scores based on tissue integrity, color (i.e., bleaching) and polyp behavior. treatment concentrations.
2. Porphyrin quantification in coral tissues. The porphyrin (heme) biosynthetic pathway is a basic macrocyclic molecule found in most major metabolic pathways and is susceptible to various anthropogenic toxicants. These can affect different enzymatic steps in the pathway and depending on which step is affected, can lead to either an accumulation or depression in levels of porphyrin precursor species.
3. DNA lesion accumulation by enumerating abasic sites as a measure of genotoxicity.
4. Histology and transmission electron microscopy (TEM, only for TNT as a case study). Histological examination was used to determine tissue-level pathologies while TEM was used to examine the cellular ultrastructural feature for any cellular pathologies.

3.6.2 Toxicity of Munitions Compounds to Coral Fragments and Coral Cells

Based on comparisons of LC50 values, picric acid was consistently the most toxic (lowest LC50) of the compounds tested, except for *Pocillopora damicornis* gastrodermal cells exposed in light conditions in which TNT had the lowest LC50 value. In this case, the LC50 values were very close (15.3 vs 22.1 µg/L), thus reversing their rank order positions. The nitrotoluenes ranked next with TNT being the most toxic followed by 2,4-DNT and 2,6-DNT being the least toxic of the three compounds.

TNT was used as a case study that included multiple analyses. Significant toxic effects in *Porites divaricata* fragments were observed. Cell toxicity assays showed significant ($p < 0.05$) effects across a range of TNT concentrations, overlapping those used for the fragment dosing. Significant ($p < 0.05$) changes at concentrations of 100 µg/L and higher were documented in visual physio-scoring of changes in polyp behavior, tissue integrity and necrosis. Histopathological changes were also seen along a gradient of concentrations with severe tissue disruption and necrosis observed at the 25,000 µg/L concentration (50,000 µg/L treatment not analyzed because of catastrophic tissue loss). TEM confirmed ultrastructural changes were also occurring, affecting gastrodermal and epidermal cells. Cellular physiological measures showed a depression in total porphyrin levels at 2,500 µg/L TNT following 24 h of exposure, indicating generalized metabolic disruption. Adverse effects on *Symbiodinium* cell growth and photosynthetic efficiency were found at concentrations as low as 250 µg/L TNT.

RDX was tested at concentrations as high as 10,000 µg/L (10 mg/L) with only 25-30% mortality achieved in the cell toxicity assay. HMX was tested at concentrations as high as 100,000 µg/L (100

mg/L). Even though this is above its reported solubility in seawater, a 30-35% level of mortality was achieved. The observed mortality was insufficient for calculating median lethal effect concentration, thus toxicities of RDX and HMX could not be ranked. It does appear, however, that RDX and HMX are far less toxic than the other MCs. Summaries of no observed effect concentrations (NOECs), lowest observed effect concentration (LOEC) can be found Table 3-3 and EC50 and EC20 in Table 3-4. It should be noted that though our experimental designs were USEPA compliant, subsequent experience with other chemicals have caused us to reconsider the methods used to create the treatments (i.e., directly in pure artificial seawater). We now believe that a 'CDOM' (color dissolved organic matter) found to varying extents in natural seawater, should have been considered as a 'carrier' for inclusion in the treatment solutions (or another analytical equivalent carrier). Therefore, the MC (particularly RDX and HMX) may not have been as available as first thought. This is of particular concern with compounds of low solubility in water.

3.6.3 Photo-enhanced Toxicity of TNT

The photo-enhanced toxicity of TNT was tested with *Pocillopora damicornis* and *Porites divaricata* calicoblast and gastrodermal cells in a 4 h exposure in either light or dark conditions. For *P. damicornis*, the results indicate that both calicoblast and gastrodermal cells were more sensitive to TNT exposure in the light than in the dark, with calicoblast LC50 values approximately 100-fold less (16 vs 1,582 µg/L) than for cells exposed in darkness. For *P. divaricata*, the results indicate that light had little effect on the LC50 for the calicoblast cells whether exposed in light or dark conditions (716 vs 968 µg/L), but there was an approximate 20-fold increase in toxicity for gastrodermal cells exposed to TNT in light conditions vs dark (54 vs 1,196 µg/L). These data are important in recognizing differences in species sensitivity (as well as cell type differences among species) and the relevance of evaluating multiple species for ecological relevance.

3.6.4 Species Sensitivities to 2,6-DNT

Three species and two cell types from each were tested to determine if they exhibited differential sensitivity among the species and cell types to 2,6-DNT exposure in light conditions. The results show very markedly a difference in species response as well as a segregation of cell type responses that correspond to each species' relative sensitivity to 2,6-DNT exposure. *Pocillopora damicornis* was the most sensitive of the three species, followed by *Porites divaricata* and the least affected by this compound was *Porites lobata* (Table 3-3 and Table 3-4). It is of interest to note that *P. lobata* is a mounding coral while the other two are branching species. The relevance of mounding vs branching species to susceptibility to MC exposure could not be determined by these experiments. However, these findings are the first to use an *in vitro* coral cell-based toxicity test for dose-response characterization and comparisons among these three shallow water coral species to 2,6-DNT. Finding differing responses among the three species is important because

this begins to lay a foundation for predicting possible ecological impacts and risk that may differ across sites depending on the species present at any particular reef site.

3.6.5 Effect of MC on the Coral Endosymbiotic Dinoflagellate, *Symbiodinium*

Seven MCs were tested in static 96 h *Symbiodinium* sp. Clade B cell culture toxicity assays. These included six nitrotoluene compounds: TNT, the parent compound, three dinitrotoluene compounds, including two of its major breakdown products, 2,4-DNT and 2,6-DNT and a minor isomer 2,3-DNT; one nitrotoluene, 4-NT; one aminodinitrotoluene, 2-ADNT; and one nitramine, RDX. Comparisons of relative toxicity among these MCs were evaluated with two physiological endpoints, cell growth and photosynthetic efficiency. Both endpoints gave similar rankings for relative toxicities (Table 3-3 and Table 3-4); however, TNT's relative position in toxicity changed depending on the physiological endpoint. Comparisons of EC50 values based on *Symbiodinium* sp. cell growth ranked TNT as the most toxic and 4-NT the least toxic of the nitrotoluenes. RDX exposures had no significant effect on cell growth at any concentration tested up to 15,000 µg/L, which approaches its solubility in seawater (19,770 µg/L at 25°C). Effects on photosynthetic efficiency were similar to those for growth; however, 2,3-DNT appeared to cause the most significant effects on this parameter. RDX had no effect on photosynthetic efficiency.

3.6.6 Correlation of Cell-based Assays with Responses of Intact Coral Fragments.

TNT and RDX was used to test how well the *in vitro* cell toxicity assays reflect responses of intact coral. Realizing coral cells are much more sensitive to toxicants than intact organisms, a correction factor is necessary to translate coral cell mortality into potential mortality of coral fragments. A regression analysis with data from *Porites divaricata* calicoblast and gastrodermal cells (both in light and dark exposure conditions) and intact *P. divaricata* fragments exposed for 96 h to TNT showed that strong positive relationships existed when *in vitro* cell mortalities were regressed against coral fragment necrosis. Each of the regression models performed very well in every case ($p < 0.05$, $r^2 > 0.95$) and each followed the normal distribution. Thus, *in vitro* cell mortality may be used to successfully predict coral fragment necrosis.

3.6.7 Conclusions

- Differential species response was observed, with *Pocillopora damicornis* more sensitive overall than *Porites divaricata* and *Porites lobata*.
- Differential cell type response was observed if exposure was in the dark vs light, with gastrodermal cells of both species, generally more sensitive than calicoblast cells, but responses were species dependent.

- Picric acid was most toxic but similar LC50s to TNT (ppb range), 2,4 DNT more toxic than 2,6 DNT (ppm range). LC50s could not be calculated for RDX or HMX because of low toxicity.
- *In vitro* coral cell assay using mortality is a good indicator for coral fragment necrosis.

Table 3-3. Summary of no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) across all coral experiments. Blanks indicate that testing was not performed.

Species	Biological Endpoint	Exposure Condition	Exposure Duration	Statistical Endpoint	Compound Tested (µg/L)								
					TNT	2,3 DNT	2,4 DNT	2,6 DNT	4-NT	2-ADNT	RDX	HMX	Picric Acid
<i>Porites lobata</i>	Calicoblast	Light	4 h	NOEC				500					
				LOEC				2,500					
<i>Porites lobata</i>	Gastrodermal	Light	4 h	NOEC				25					
				LOEC				100					
<i>Porites divaricata</i>	Calicoblast	Light	4 h	NOEC	100		0.5	25			100	1,000	1
				LOEC	500		5	100			500	10,000	10
<i>Porites divaricata</i>	Calicoblast	Dark	4 h	NOEC	100								
				LOEC	500								
<i>Porites divaricata</i>	Gastrodermal	Light	4 h	NOEC	25		25	5			500	1,000	<1
				LOEC	100		100	25			1,000	10,000	1
<i>Porites divaricata</i>	Gastrodermal	Dark	4 h	NOEC	25								
				LOEC	100								
<i>Porites divaricata</i>	Fragment Porphyrin	Diurnal 16:8 D:L	24 h	NOEC	500								
				LOEC	2,500								
<i>Porites divaricata</i>	Fragment Porphyrin	Diurnal 16:8 D:L	96 h	NOEC	500								
				LOEC	2,500								
<i>Pocillopora damicornis</i>	Calicoblast	Light	4 h	NOEC	<0.5		5	100			10	1,000	<1
				LOEC	0.5		25	500			100	10,000	1
Pocillopora damicornis	Calicoblast	Dark	4 h	NOEC	25								
				LOEC	100								
<i>Pocillopora damicornis</i>	Gastrodermal	Light	4 h	NOEC	0.5		0.1	5			1,000	10	10
				LOEC	5		0.5	25			10,000	100	100
<i>Pocillopora damicornis</i>	Gastrodermal	Dark	4 h	NOEC	0.5								
				LOEC	5								
<i>Pocillopora damicornis</i>	Fragment Porphyrin	Diurnal 16:8 D:L	96 h	NOEC		162					>16,000		
				LOEC		292					>16,000		
<i>Symbiodinium Clade B</i>	Dinoflagellate Growth	Diurnal	96 h	NOEC	<250	1,250	310	12,500	25,000	630	>15,000		
				LOEC	250	2,500	630	25,000	50,000	1,250	>15,000		
<i>Symbiodinium Clade B</i>	Dinoflagellate Photosyn. Effic.	Diurnal	96 h	NOEC	<250	<160	630	12,500	25,000	<630	>15,000		
				LOEC	250	160	1,250	25,000	50,000	630	>15,000		

Table 3-4. Summary of lethal (LC) and effect (EC) concentrations across all coral experiments. DMF = Data model failed. Blanks indicate that testing was not performed.

Species	Biological Endpoint	Exposure Condition	Exposure Duration	Statistical Endpoint	Compound Tested (µg/L)								
					TNT	2,3 DNT	2,4 DNT	2,6 DNT	4-NT	2-ADNT	RDX	HMX	Picric Acid
<i>Porites lobata</i>	Calicoblast	Light	4 h	LC50				105,124					
				LC20				948					
<i>Porites lobata</i>	Gastrodermal	Light	4 h	LC50				4,748					
				LC20				216					
<i>Porites divaricata</i>	Calicoblast	Light	4 h	LC50	716		5,818	16,557			DMF	DMF	60.4
				LC20	60.5		79	631			DMF	DMF	10
<i>Porites divaricata</i>	Calicoblast	Dark	4 h	LC50	968								
				LC20	32.6								
<i>Porites divaricata</i>	Gastrodermal	Light	4 h	LC50	54		3,123	3,699			DMF	DMF	20.5
				LC20	0.36		52	137			DMF	DMF	2.1
<i>Porites divaricata</i>	Gastrodermal	Dark	4 h	LC50	1,196								
				LC20	21								
<i>Porites divaricata</i>	Fragment Porphyrin	Diurnal 16:8 D:L	24 h	EC50	5,416								
				EC20	DMF								
<i>Porites divaricata</i>	Fragment Porphyrin	Diurnal 16:8 D:L	96 h	EC50	DMF								
				EC20	DMF								
<i>Pocillopora damicornis</i>	Calicoblast	Light	4 h	LC50	16		1,284	11,075			DMF	DMF	10.5
				LC20	1.85		15	463			DMF	DMF	1.2
<i>Pocillopora damicornis</i>	Calicoblast	Dark	4 h	LC50	1582								
				LC20	200								
<i>Pocillopora damicornis</i>	Gastrodermal	Light	4 h	LC50	15.3		565	1,844			DMF	DMF	22.1
				LC20	2.15		2	71			DMF	DMF	3.7
<i>Pocillopora damicornis</i>	Gastrodermal	Dark	4 h	LC50	140								
				LC20	12.7								
<i>Pocillopora damicornis</i>	Fragment Porphyrin	Diurnal 16:8 D:L	96 h	EC50		DMF							
				EC20		DMF							
<i>Symbiodinium Clade B</i>	Dinoflagellate Growth	Diurnal	96 h	EC50	544	2524	1,315	22,292	116,083	4,059	DMF		
				EC20	17	1275	314	4,135	35,715	915	DMF		
<i>Symbiodinium Clade B</i>	Dinoflagellate Photosyn. Effic.	Diurnal	96 h	EC50	7039	2810	4,814	45,516	137,902	10,206	DMF		
				EC20	1908	2520	1,380	17,749	62,814	1,801	DMF		

3.7 *Bioaccumulation and Toxicity of Energetic Compounds in Terrestrial Biota and Relevance to Aquatic and Wetland Environments*

Issues associated with environmental release of energetic compounds used in legacy munitions have become an emerging concern where munitions have been disposed of or released in aquatic environments. As data are collected to evaluate the potential for exposure, studies conducted with these substances for addressing terrestrial releases can have useful applications in aquatic environments such as wildlife inhabiting wetlands or nearshore environments (Bruder et al. 2018) where munitions are present as a result of military activities may be exposed to MC.

This section provides a brief overview of the effects from environmental releases of MC on terrestrial biota, including plants, wildlife and soil invertebrates. The toxicity of chemicals of military concern to terrestrial wildlife was extensively addressed in Williams et al. (2015) and an overview of the effects of energetic compounds on soil invertebrates and plants was provided in Kuperman et al. (2009) and Lotufo (2017) and is summarized below.

Studies show energetic compounds have low potential to bioaccumulate in plants, soil invertebrates and terrestrial vertebrates. Though accounts exist where concentrations of explosives or metabolites have been found in tissue, no data have been found to suggest body burdens exceed excretion rates or could constitute an unacceptable risk to wildlife. RDX has the greatest potential to bioaccumulate in plants, but only as high as the evapotranspiration rate in specific tissues. This is likely to be less for plants in aquatic environments.

In mammals, acute effects from nitroaromatic and nitramine exposures include neurological effects (e.g., convulsions) often observed prior to mortality. Other than sensitization for some compounds, triazoles tend not to be acutely toxic. Sublethal effects from repetitive exposures to nitroaromatics and other nitrate-containing explosives (NO₂) exhibit toxicity similar to nitrates alone – specifically, hemolytic effects such as reductions in red blood cells, hemoglobin and packed cell volume (anemia). Repetitive exposures to nitroaromatics and 3-nitro-1, 2, 4-triazol-5-one (NTO) have also been reported to cause male reproductive effects (e.g., testicular atrophy) without evidence of endocrine disruption. In birds, differences in the refractory nature of avian red blood cells appear to be resilient to this effect. A common biomarker of TNT exposure for sublethal toxicity is the appearance of chromatouria in animals.

Mammalian toxicity of nitramines is predicted by absorption potential from point of exposure. RDX is quickly absorbed through the gut into systemic circulation and appears to pass through the blood-brain and blood-testis barriers easily. HMX is poorly absorbed through the gut in monogastric species; however, it can be absorbed under longer gut retention times in hindgut fermenting species and likely ruminants.

Nitrate esters are known to have vasodilatory effects, and some have been tested and used therapeutically for cardiac angina (e.g., PETN, NG). Mechanism for this effect is thought to be linked to liberation of nitric oxide following metabolism. Few other adverse effects have been described for nitrate esters. The data environmental effects of triazoles is limited at present as they are being used in recent insensitive munition (IM) formulations. They show reproductive effects or testicular effects in animals.

Toxicity of metalloids is largely attributed to the metals themselves. As they often constitute the primer portion of the munition, the quantities used are relatively small and hence are released at low levels in the environment and are not expected to contribute significantly to environmental release or exposure. This may not be the case for specific occupational conditions.

The nitramine explosives RDX and HMX have not been shown to cause substantial adverse effects to terrestrial plants, even at concentrations exceeding 9,000 mg/kg. These compounds are highly mobile within plants and concentrate in leaf and flower tissues, posing potential exposure risks of food-chain transfer to higher trophic levels. Nitroaromatic explosives, especially TNT transformation products, were substantially more toxic to terrestrial plants, as significant decreases in growth and survival in a variety of species typically occurred at concentrations in soils ranging from 10 to 100 mg/kg.

Differently from soil microbes and plants, some soil invertebrates have been shown to be strongly affected by RDX and HMX (e.g., decreased reproduction in earthworms at 1–5 mg/kg for RDX), while others, such as potworms, were insensitive to exposure to these compounds (e.g., no mortality at >1,000mg/kg for RDX). The toxicity of TNT-spiked soil to soil invertebrates was widely variable, with toxicity benchmarks varying with soil type, test species, and exposure type. Mortality typically occurred within the 100–500 mg/kg range.

In summary, the low probability of exposure through environmental breakdown and dilution potential, low potential for bioaccumulation, and low probability for sustained repetitive exposures to legacy explosive fills is unlikely to result in unacceptable risk to terrestrial biota at the majority of sites. However, distribution of MC is typically spatially heterogeneous (Pichtel 2012) and high concentrations in localized areas may result in adverse toxicological effects to organisms inhabiting those area.

3.8 Removal Challenges/Blast Risk

The main focus of this presentation was to consider what happens next at a munitions response (MR) site once the determination is made that munitions are present. By default, given sufficient time and appropriate conditions, it is presumed all MC contained within a munition will eventually be released to the environment.

Underwater actions related to MEC to date, however, are generally focused on explosive hazard not MC. Whether 200-year-old cannonballs or modern munitions with explosive components, there is no time when a munitions item becomes “safe”. MR drivers include both constituents and explosive hazards. The explosive hazards are acute, depend on munition type and environmental factors. Further, water is an essentially incompressible media, and transmits blast effects for exceptional distances compared to on land, making safe swimmer distances from a BIP remedy as long as a mile.

The current remediation tools available for underwater MEC are summarized in Figure 3-9 and illustrated in Figure 3-10. Costs for many of these approaches are conservatively estimated to be 10x of those for terrestrial anomalies. These can be broken down more simply into *in situ* approaches (e.g., BIP, encapsulation, use controls) and *ex situ* approaches (e.g., diver recovery, dredging, ROV) that have been fielded the most to date. These tools are shown to be somewhat successful, but none have been identified as the ideal solution. For example, BIP can lead to local ecological consequences, even with the use of bubble curtains due to the effects of blast overpressure. Examples of use control include warning signs on land, warning buoys in affected embayments, and warning notes on nautical charts. Dredging high-density areas is a rational approach followed by resurveying the site with geophysics to verify effectiveness.

In addition to the above current tools, several future remediation alternatives are anticipated. These include underwater UXO neutralization by explosively formed plasma (Douglas and Emery 2019, [ESTCP MR-201611](#)) and demonstration of a cut and capture waterjet cutting system technology (Schmidt 2020, [ESTCP MR18-5116](#)). Underwater, waterjet cutting would allow for safe removal of the explosive fill without the need for detonation and allow for the empty munition body to remain within a reef structure. Other technologies discussed included biodegradation and use of advanced manipulators/ROVs that can have much more of the required precision over current ROV technologies to potentially remove munitions.

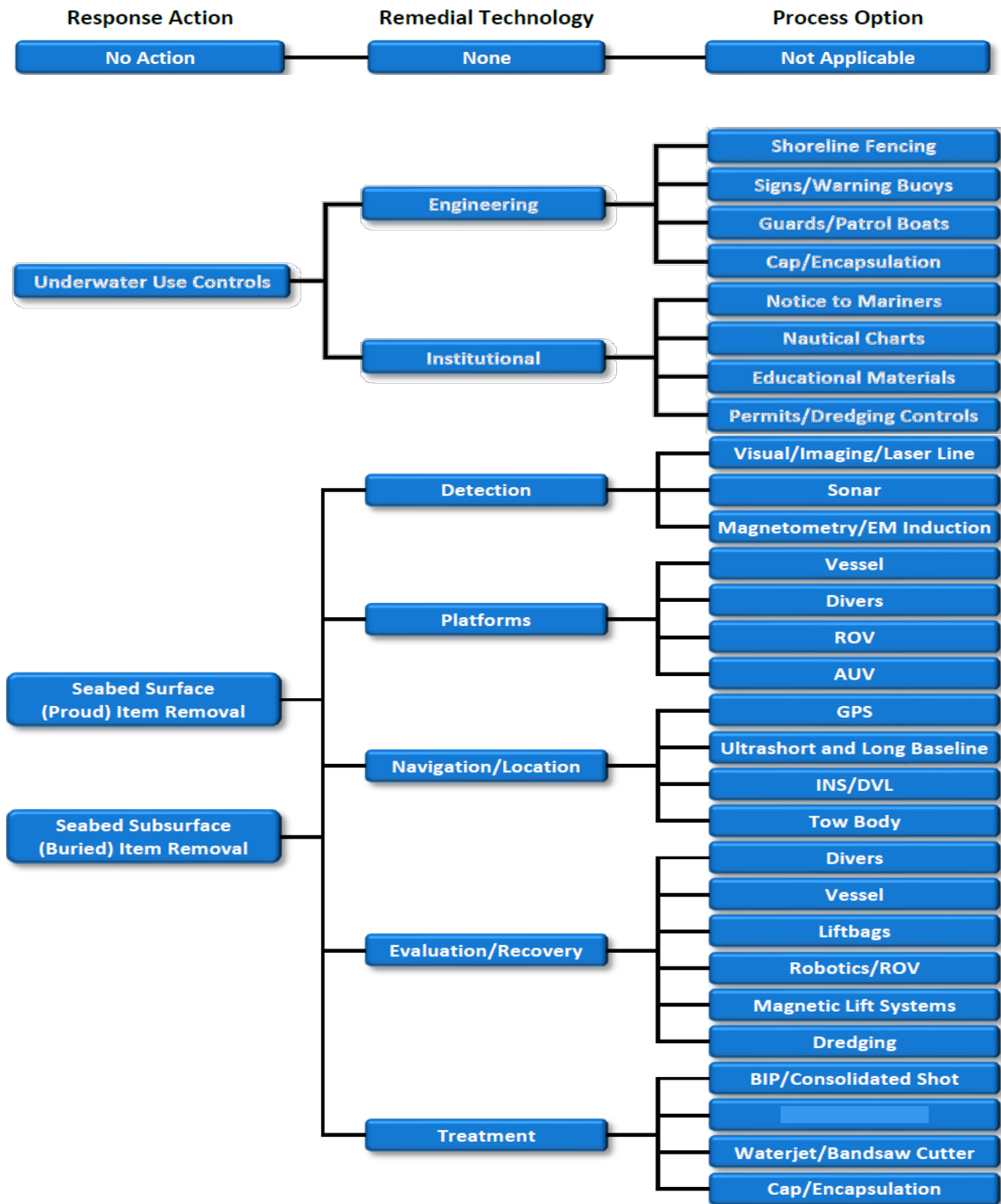


Figure 3-9. Current investigation/remediation tools used or being evaluated for underwater MEC.

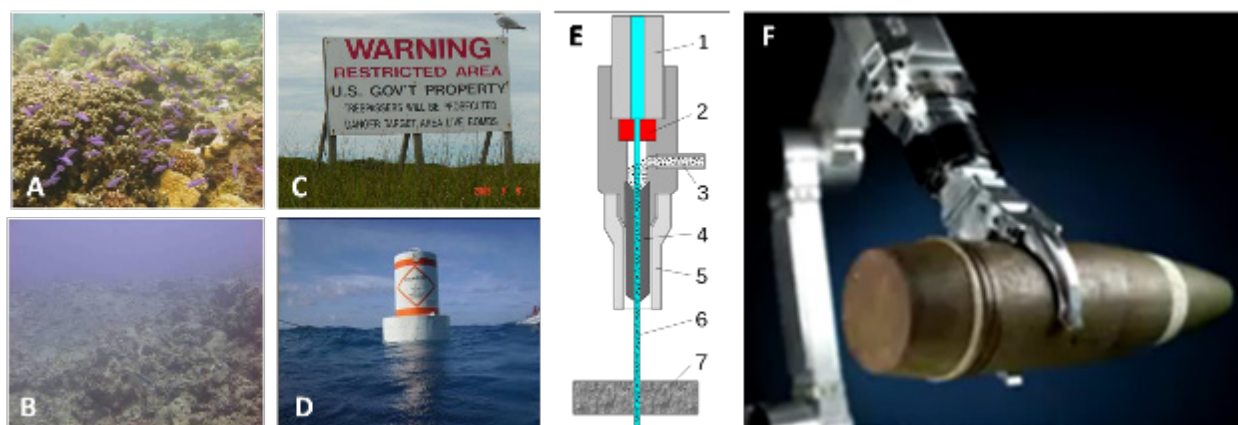


Figure 3-10. Examples of current and future remediation tools, including views associated with BIP before (A) and after (B) remediation, various forms of LUC (C,D), waterjet cutting technology (E), and use of (F) advanced manipulators and ROVs.

4.0 SITE STUDIES

4.1 Overview of MC in Water, Sediment and Biota at UWMM Sites

4.1.1 MC in the Water Column

For the following UWMM sites, water sampling in the proximity of munitions resulted in no detections of MC in the samples collected:

- Ordnance Reef study sites: Laboratory reporting limits (LRLs) ranged from 0.1 to 1.4 µg/L (UH 2014a).
- HUMMA study sites: LRLs ranged from 0.14 to 43 µg/L (UH and Environet 2010).
- Shipwrecks located south of Halifax, Canada: method detection limit (MDL) = 0.001 µg/L (Ampleman et al 2004).
- Swedish lakes and coastal sites: Information on detection limits not found (Sjostrom et al. 2004).
- Lake Randsfjorden (Norway): Information on detection limits not found (Rossland et al. 2010).

For several UWMM sites, water sampling in the proximity of munitions resulted in the detection of one or more of the MC analyzed for in at least one sample, as detailed below:

- Point Amour (Labrador, Canada): The concentration of TNT in water samples collected near the wreck of the HMS Raleigh were 0.002 µg/L or lower (Ampleman et al. 2004).
- Lake Mjøsa (Norway): A 2001 survey did not find detectable concentrations of MC in the water at Mjøsa (Norway) (Rossland et al. 2010). Sampling of water from Mjøsa's deepest point "station Skreia" in 2003 resulted in the detection of TNT at 0.17 µg/L and DNB at 0.18 µg/L.
- Coastal fortifications in Norway: MC were not detected in any of the seawater samples collected at the Solstrand site (Rossland et al. 2010). The single water sample collected near the German anchored mine at the Tælavåg site after transport to a safe location and before detonation, contained detectable concentrations of RDX (12.7 µg/L) and HMX (0.62 µg/L). Those explosives were not detected in the three samples taken after detonation of the mine, but TNT was detected in all samples at 0.2, 0.14 and 0.1 µg/L while 2-ADNT and 4-A-26DNT were detected in one sample at 0.1 and 0.32 µg/L.
- Halifax Harbor: In water samples from 0.3 to 3 m downcurrent from UWMM and surface water above UWMM, MC were detected at a frequency ranging from 7 to 50%. Maximum concentrations ranged from 1.2 to 123 µg/L (Rodacy et al. 2001) (Table 4-1).

Table 4-1. Detection frequency and range of measured concentrations of MC in the water collected at Halifax Harbor (Halifax, Canada).

MC	Detection frequency (%) (n = 36)	Range of concentrations (µg/L)
TNT	25	0.01 – 14.2
2-ADNT	38	0.04 – 108
4-ADNT	46	0.03 – 123
2,4-DNT	50	0.02 – 3.14
2,6-DNT	8	1.7 – 2.0
TNB	9	0.10 – 1.24
DNB	7	1.02 – 5.9

- Bahia Salina del Sur (Vieques, PR): Porter et al. (2011) reported the concentration of MC in water samples were collected at various distances from a 2,000 lb. general purpose (GP) bomb. For samples taken from within the solution cavity of the bomb, TNB, DNB, TNT, 2,4-DNT + 2,6-DNT, 4-NT, 2-NT, and RDX were detected at extremely high concentrations ranging from 4,120 to 85,700 µg/L. Concentrations for those MC decreased dramatically when samples were taken adjacent (i.e., 10 cm) from the breach, with concentrations ranging from 3.3 to 107 µg/L. According to Barton and Porter (2004), samples taken at 1 m from the bomb contained concentrations of TNT measuring 17.7 and 7.87 µg/L.
- Bahia Salina del Sur (Vieques, PR): For [ESTCP project ER-201433](#) (Rosen et al. 2016, 2017a), concentrations were reported for two sampling rounds of grab samples of water and also reported as estimated time-weighted average (TWA) concentrations based on concentrations measured in POCIS. Grab sample collection and POCIS placement were near UWMM, some with visible breaches. Detection frequency for grab samples and POCIS was relatively low (Table 4-2). Passive sampler-estimated TWA concentrations were 3.8 µg/L for TNT (1 location out of 14) and an order of magnitude or more lower for other MC (Table 4-2). Concentrations measured in grab samples were 4.5 and 7.5 µg/L for TNT (1 location out of 14) but much lower for other MC (Table 4-2). Concentrations of MC in the water column from 15 passive samplers placed in a grid pattern approximately equidistant from each other represented the majority of the site. Only TNT and RDX were detected, and the frequency of detection was of 7 and 40%, respectively. TNT was detected in one location at 0.006 µg/L, and RDX in 6 locations at concentrations ranging from 0.004 to 0.012 µg/L (Table 4-2).

Table 4-2. Detection frequency and concentrations of MC in the water column near UWMM as measured by passive samplers and grab samples at grid locations as measured by grab samplers at the Isla de Vieques Bombing Range site (PR).

MC	Samples near UWMM				Grid samples	
	Passive sampler		Grab samples		Passive sampler	
	Detect. freq. (%) (n = 14)	Conc. (µg/L)	Detect. freq. (%) (n = 30)	Conc. (µg/L)	Detect. freq. (%) (n = 15)	Conc. (µg/L)
TNT	7	3.8	7	4.5; 7.5	7	0.006
2-ADNT	14	0.01; 0.26	7	0.004; 0.09	0	ND
4-ADNT	7	0.32	7	0.02; 0.07	0	ND
2,4-DNT	7	0.07	7	0.01; 0.02	0	ND
2,6-DNT	0	ND	0	ND	0	ND
TNB	0	ND	7	0.02; 0.04	0	ND
3,5-DNB	7	0.09	0	ND	0	ND
3,5-DNA	7	0.02	0	ND	0	ND
RDX	79	0.005 to 0.013	10	0.02; 0.03; 0.05	40	0.004 to 0.012

- Kolberger Heide: For a sample collected directly at the munition surface (i.e., at 0 cm from the solid surface), TNT was 3,100 µg/L. Concentrations declined rapidly away from the munition surface, to 16 µg/L at a 1 cm distance and 3.3 µg/L 50 cm away. Samples collected during follow-up sampling events showed less striking decreases along a similar transect (maximum measured TNT was 50 µg/L). RDX and DNB showed a similar trend, but the concentrations were lower (~1–10 µg/L). The lowest concentrations were consistently observed for RDX, generally 1–2 µg/L or less, and profiles often did not show a clear decreasing trend away from the surface. Trends were also less clear for DNB, although concentrations were as high 22 µg/L (Beck et al. 2019).

Water sampling from the water column above or at the bottom, but not targeting proximity to munitions, were conducted for a several of UWMM sites as detailed below:

- Lakes Thun and Brienz (Switzerland): Water was sampled at various depths (up to 255 m) at Swiss lakes reported HMX, RDX, and PETN at 0.0004 µg/L or lower concentrations in all samples (Ochsenbein et al. 2008). Concentration profiles obtained during a 12-month period showed a homogeneous distribution of the explosives. Consequently, UWMM at the bottom of the lakes does not seem to be responsible for the contamination of the water column at the lakes. HMX, RDX, and PETN were detected in lake tributaries at concentrations as high as 0.0009 µg/L, which showed that tributaries seem to play an important role as external sources for the explosives found in the lakes (Ochsenbein et al. 2008).
- Lakes Thun and Lucerne (Switzerland) (Estoppey et al. 2019). Passive samplers (Chemcatcher and POCIS) deployed at the deepest points of each lake basin (200m depth) generated TWA

concentrations of about 0.0004 µg/L for RDX and HMX and 0.0001 µg/L for PETN at Lake Lucerne. In Lake Thun, TWA concentrations of HMX, RDX, and PETN were lower and most of the time below the limit of quantitation (LOQ) (0.00002 – 0.0003 µg/L). In both lakes, nitroaromatic concentrations were below LOQ (0.00002 – 0.01 µg/L). The LOQ and detected concentrations reported for grab samples were generally lower, but only by a few fold, than those for passive samplers.

- Kolberger Heide: TNT and DNB were detected at low concentrations (0.001–0.015 µg/L) and RDX, TNB, DNA, 2A-4,6-DNT, and 4A-2,6-DNT were present at lower concentrations (< 0.002 µg/L) levels of in the waters at Kolberger Heide (Gledhill et al. 2019). RDX, DNB, TNT, 2A-4,6-DNT, and 4A-2,6-DNT were detected in every one of the 12 samples analyzed.

4.1.2 MC in Sediment

For the following UWMM sites, sediment sampling resulted in no detection for the MC analyzed for in all samples:

- Shipwrecks located south of Halifax, Canada: MC were not detected in any of the sediment samples at concentrations exceeding their detection limit (DL) (0.1 mg/kg) (Ampleman et al. 2004).
- Swedish lakes and coastal sites: Neither TNT nor its degradation products were detected in any of the sediment samples at concentrations exceeding their DL. Information on DL was not found (Sjostrom et al. 2004).
- Beaufort's Dyke (North-East Atlantic): TNT, RDX, tetryl and NG were below the level of detection for all sediment samples (Aberdeen Marine Laboratory 1996). Information on DL was not found.
- Bahia Salina del Sur (Vieques, PR): For [ESTCP project ER-201433](#) (Rosen et al. 2017a), the concentrations of MC were below detection for all porewater and sediment samples. Quantitation limits ranged from 0.009 to 0.054 µg/L for porewater samples and from 2 to 10 µg/kg for sediment samples.

For several UWMM sites, sediment sampling resulted in the detection of one or more MC in at least one sample, as detailed below:

- Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA): For the subsurface samples, concentrations were below 0.005 mg/kg for all MC detected except NC (1.6-31 mg/kg) and NG (6.6 mg/kg). Surface sediments had MC concentrations below 0.005 mg/kg for TNT, 2-ADNT, 4-ADNT, 3,5-dinitroaniline, HMX, RDX, 2,4-dinitrophenol (DNP), NG, and PETN. Much higher concentrations were reported for NC (1.6-14 mg/kg) and NG (0.14-0.65 mg/kg) (NAVFAC NW 2010a).
- Ordnance Reef study sites: Concentrations near munitions were 0.03-3.3 mg/kg for 2,4-DNT, 0.098 and 0.380 mg/kg for 2,6-DNT and 0.022-0.025 mg/kg for TNB. For 2,4-DNT and TNB detected outside the DMM stratum, concentration ranges were 0.030 and 0.048 mg/kg and 0.021-0.047 mg/kg, respectively. All other MC were below their DL (0.25 mg/kg or lower) (UH

2014a). For surface sediment collected during the follow-up investigation (FUI) (UH 2014b), mostly from locations where munitions were removed during removal technology demonstration (Carton et al. 2012), 2,4-DNT, 2,6-DNT, 2-NT, 4-NT, RDX and NG were the only compounds detected. Concentrations were 0.03-110 mg/kg for 2,4-DNT; 0.07-10 for 2,6-DNT; 0.08, 1.1 mg/kg for 2-NT; 0.49 for 4-NT; 0.14 mg/kg for RDX; and 0.56, 1.7 for NG. The MC 2,4-DNT was also detected outside the DMM stratum at 0.03 and 0.06 mg/kg. All other MC were below their DL (2.5 mg/kg or lower). For the location where the highest concentration was reported (110 mg/kg for 2,4-DNT), the concentration decreased substantially with increasing distance (6.7 mg/kg at 0.9 m and 2.3 mg/kg at 1.8 m).

- HUMMA study sites: MC were not detected in any of the sediment samples collected during the 2009 HUMMA sampling event. The DL was 0.1 mg/kg or lower. (UH and Environet 2010; Briggs et al. 2016). Samples collected during the 2012 HUMMA sampling event resulted in detection of a single energetic MC, 4-NT, at 0.09 and 0.12 mg/kg, in only 2 of the 121 samples analyzed. The DL for MC ranged from 0.078 to 0.080 mg/kg (UH and Environet 2016; Briggs et al. 2016).
- Former Seattle Naval Supply Piers 90 and 91: For surface sediment, concentrations were 0.2–0.97 mg/kg for 2,4-DNT; 0.12 mg/kg for 2,6-DNT; 0.58, 0.59 mg/kg for RDX; 0.003 mg/kg for picric acid; and 0.23 mg/kg for tetryl. All other MC were below the MDL of 0.4 mg/kg or lower (USACE 2013).
- Point Amour (Labrador, Canada): For sediment samples collected near the wreck of the HMS Raleigh, only HMX was detected (<0.15 mg/kg). All other MC were below the DL of 0.1 mg/kg (Ampleman 2004).
- Coastal fortifications in Norway: For the Solstrand site, one of the four sediment samples collected at sea contained TNT (0.07 mg/kg). For the three sediment samples collected under the pier, three samples contained TNT (0.05, 0.07, and 0.08 mg/kg), and one sample contained HMX (0.06 mg/kg). TNT and RDX HMX were the only MC detected in the two sediment samples collected near the detonation site of the ship wreck *DS Selma* (0.31 and 0.41 mg/kg TNT and HMX in one sample, and 0.14 and 0.12 mg/kg TNT and HMX in the other sample). All other MC were below their DL (Rossland et al. 2010).
- Halifax Harbor: For surface sediment collected from up to 3 m down-current from munitions at Bedford Basin, maximum concentrations were 0.17, 0.09, 0.55, 0.56, 0.85, 0.09, and 0.09 mg/kg for TNT, 2-ADNT, 4-ADNT, 2,4- and 2,6- DNT, TNB, and DNB, respectively (Rodacy et al. 2001).
- Bahia Salina del Sur (Vieques, PR): Barton and Porter (2004) and Porter et al. (2011) reported the concentration of MC in sediment samples were collected at various distances from a 2,000 lb. GP bomb. For samples taken adjacent to the bomb, TNT, TNB, DNB, 2,4-DNT + 2,6-DNT, 4- and 2-NT, and RDX were detected at concentrations ranging from 5.39 to 19,333 mg/kg. TNT was reported at 19,333 mg/kg at the breach of the bomb, but at orders of magnitude lower concentrations at increasing distances (0.506 mg/kg and 0.404 mg/kg at 0.01 and 0.1 m, respectively) and below the DL (value not provided) at 1 m and beyond. MC other than TNT were not detected at distances of 0.01 m and greater from the bomb.

4.1.3 MC in Biota

For several UWMM sites, biota sampling resulted in the detection of one or more MC analyzed in at least one sample, as detailed below:

- Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA): For Operable Unit 2 (NAVFAC NW 2010b), 3-NT, TNB, nitrobenzene, picric acid, picramic acid, and NG were detected in the resident biota. For Operable Unit 1 (NAVFAC NW 2011), 2,4-DNT, 2,6-DNT, and TNB were detected in the resident biota (Table 4-3).

Table 4-3. Detection frequency and concentrations of MC in the biota sampled from Jackson Park Housing Complex/Naval Hospital Bremerton Superfund Site (WA) Operable Unit 2 and Operable Unit 1.

MC	Biota	Number of samples	Detect. freq. (%)	Conc. or range of conc. (µg/kg)
Operable Unit 2				
3-NT	Flounder	6	17	460
4-NT	Sea cucumber	6	17	330
TNB	Crab	6	17	2.2
Nitrobenzene	Crab	6	50	480–580
	Sea cucumber	6	50	670–950
	Flounder	6	50	220–320
Picric acid	Sea cucumber	6	33	0.35–041
Picramic acid	Clam	6	17	10.9
	Crab	6	17	5.9
NG	Clam	6	17	290
	Sea cucumber	6	17	520
	Flounder	6	17	650
Operable Unit 1				
2,4-DNT	Clam	15	20	47–53
2,6-DNT	Clam	15	13	77–130
TNB	Clam	15	13	7,300–7,800

- Ordnance Reef study sites: For biota collected from the DMM stratum in 2009 (UH 2014a), no MC was detected in any Kona crab or seaweed samples. HMX was detected in one octopus sample at 62 µg/kg. Concentrations in fish (34 samples) were 37-180 µg/kg for 2,4-DNT (8 samples); 46 and 55 µg/kg for 2-NT (2 samples); 92 µg/kg for 4-NT (1 sample); 45, 53 for 3,5-dinitroaniline (2 samples); 1,600 µg/kg RDX (1 sample); 37-420 µg/kg for HMX (11 samples) and 390 and 850 µg/kg for tetryl (2 samples). For biota collected from the DMM stratum

during the FUI (UH 2014b), no MC was detected in any Kona crab, octopus, or seaweed sample, and 2,4-DNT, 2,6-DNT, and TNB were detected in fish samples with a frequency of up to 11% (for TNB). Concentrations in fish were 39 µg/kg for 2,4-DNT; 140 µg/kg for 2,6-DNT; and 53–62 µg/kg for TNB.

- HUMMA study sites: MC were not detected in shrimp or fish sampled at sea disposal site Hawaii (HI-05) in 2009 (UH and Environet 2010). For shrimp trapped and sampled in 2012, 4-ADNT was detected at estimated concentrations (33 µg/kg and 45 µg/kg) in two samples collected at a conventional munitions site (7% detection frequency) (Koide et al. 2016).
- Bahia Salina del Sur (Vieques, PR): Barton and Porter (2004) and Porter et al. (2011) reported the concentration of MC in biota collected near a 2000-lb bomb. TNT was found in the feather duster worm (40,200 mg/kg), the sea urchin (721 mg/kg), and the mountainous star coral (600 mg/kg). 1,3,TNB was detected in the damselfish sample (4.6 mg/kg), the feather duster worm (23.9 mg/kg), and the mountainous star coral (250 mg/kg); 2,4 + 2,6-DNT was found in the mountainous star coral (250 mg/kg). DNB was detected in the mountainous star coral (250 mg/kg) and the feather duster worm (9.5 mg/kg), that also contained 4-NT (95.5 mg/kg), explosive residues were not detected in fish and lobster samples collected near the former U.S.S. Killen. One out of six coral samples collected from the U.S.S. Killen area contained detectable TNT residues (252 mg/kg). All other coral samples contained no detectable TNT (<1.2 mg/kg) or RDX (<1.3 mg/kg).
- Kolberger Heide: For mussels deployed at the sediment surface near scattered munitions fillers, the concentrations of TNT, 2-ADNT and 4-ADNT were 31.04, 103.75 and 131.31 µg/kg, respectively. For mussels positioned 1 m above the sediment surface no TNT nor 2-ADNT could be detected, but 4-ADNT was detected at 8.71 µg/kg (wet weight) (Strehse et al. 2017). Body burden did not differ significantly regarding the distance to the mine mount or regarding the position of the mussels on the mooring. In mussels directly deployed at lumps of loose hexanite, 4-ADNT, 2-ADNT and TNT were found in total concentrations up to 260 µg/kg (Strehse et al., 2017). In the mussels deployed at the moored mines 4-ADNT was detected at up to 8 µg/kg (wet weight) (Appel et al. 2018). Mussels exposed to explosives horizontally in 30 cm intervals in a region with larger and smaller pieces of explosive material scattered on the seafloor showed the higher concentrations of TNT metabolites than mussels exposed at the moored mines. the concentrations of 4-ADNT, 2-ADNT and 2,4-DANT ranged between 70 and 145, 22 and 55 and 33 and 73 µg/kg, respectively. Body residues decreased upward in the water column (Maser and Strehse 2020). The mussel monitoring studies at Kolberger Heide showed that BIP operations, which typically leave substantial quantities of the explosive materials on the seafloor, may lead to considerably higher accumulation of TNT and its daughter compounds in the exposed mussels.
- Kolberger Heide: At the same site, a preliminary survey of resident algae and tunicates were reported as containing at varying concentrations (1–100 µg/kg RDX, DNB, NG, TNT, DNT and ADNT). A species of starfish (Asteroidea) contained the highest levels of MCs, with 24 mg/kg TNT in a specimen collected at the crater site, which could have arisen from direct contact with exposed munitions (Gledhill et al. 2019).

4.2 Ecological Risk Assessment Considerations for UWMM Sites

This section discusses the environmental risk posed by the presence of MC in water and sediment at UWMM sites through the comparison of MC concentrations with toxicity benchmarks values provided in Lotufo et al. (2017). This simplistic approach is used in screening-level risk assessment, such as that set forth in the Tri-Service Ecological Risk Assessment Working Group—*A Guide to Screening Level Ecological Risk Assessment* (TSERAWG 2008). Screening-level risk assessments (SLRAs) are performed to identify contaminants that may pose unacceptable risks and those that can be conservatively ruled out as posing an environmental concern.

Exposure estimates were based on site-specific data while effects characterization was based on effects benchmarks representing the threshold of a safe exposure levels for aquatic biota. For the risk calculation, the hazard quotient approach, which compares exposure values with toxicity benchmarks (i.e., a selected ecological screening level [ESL]), is derived using the following equation:

$$\text{HQ} = \text{Exposure value} / \text{ecological screening level}$$

The exposure value is a concentration representing exposure at the site (e.g., $\mu\text{g MC/L water}$) and the ESL is a concentration representing a safe level of exposure. Thus, for each MC and environmental medium, the hazard quotient (HQ) is expressed as the ratio of a potential exposure level to the applicable toxicity-based benchmark. Decision rules are applied to the results for interpretation of potential risks. For HQ values exceeding unity (1.0) the potential for adverse effects to the receptors of concern is concluded to be possible. In contrast, if the resulting HQ is equal to or less than unity, the potential for risks due to that chemical can be considered negligible and therefore may be dropped from further consideration of risk for that exposure pathway. The logic is supported through the consistent application of conservative assumptions, biasing towards overestimating potential risks. Because of the high level of conservatism in an SLRA, the fact that a contaminant “fails the screening” (i.e., HQ greater than 1) following an SLRA does not necessarily indicate a real risk. Conversely, a HQ less than 1 leading to contaminant being “screened out” from further consideration should convincingly indicate a lack of risk (Hill et al. 2000).

When the HQ is greater than 1, the potential for adverse effects from the MC is further evaluated using detection frequency information (TSERAWG 2008). The distribution of the chemicals present at a site or exposure area should be examined by identifying where the chemicals were and were not detected and their frequency of detection. If this evaluation indicates that the distribution of a chemical is low (i.e., it is detected in only one or a few locations) it may be reasonable to conclude that risk can be considered negligible for that exposure pathway. In

addition, when HQ is greater than 1, uncertainties will be considered, and additional lines of evidence will be used to further evaluate the potential for risks.

The discussions of potential for environmental risk at UWMM sites in this document are for the purpose of a big-picture general discussion only and not for use for actual site-specific determinations of risk.

4.2.1 Comparison of Water Concentrations with Toxicity Benchmarks

For the sites listed below, analysis of water sampled near munitions resulted in no detection for the MC analyzed. For those sites, limits of detection for MCs were lower than benchmark values derived in Lotufo et al. (2017).

- Ordnance Reef study sites: LRLs ranged from 0.1 to 1.4 µg/L (UH 2014a)
- HUMMA study sites: LRLs ranged from 0.14 to 43 µg/L (UH and Environet 2010)
- Shipwrecks located south of Halifax, Canada: MDL = 0.001 µg/L (Ampleman et al 2004)

For UWMM sites investigated for MC contamination and listed in Table 4-4, concentrations for the MC with detected concentrations were below hazardous concentration 5% (HC₅) derived in Lotufo et al. (2017), which are values derived from species sensitivity distributions representing the probability of 5% of species being affected. Provisional water quality criteria values and HC₅ values derived using no-effects concentrations are also provided in Lotufo et al. (2017) and may be used as more conservative screening benchmark values for estimating potential for adverse effects at UWMM sites.

Concentrations reported in Table 4-4 were taken at least 1 cm away from the munitions and concentrations reported for samples right at the surface of the exposed munition filling or piece, as detailed below, were excluded. For two sites, water samples were taken along a distance gradient away from a single item believed to be the source of dissolved MC to the surrounding water. Porter and Barton (2004) and Porter et al. (2011) reported the concentration of MC for samples taken at various distances away from a visible breach on a large bomb located at Bahia Salina del Sur (Vieques, PR). Beck et al. (2019) sampled water at various distances away from an exposed munition fragment in the Southwest Baltic Sea. Both studies reported concentrations in the single or double-digit mg/L range right at the surface of the exposed munition filling or piece. At both sites, the concentration of MC decreased substantially with distance. For example, the concentration of TNT collected at the munition breach was 85.7 mg/L in Bahia Salinas del Sur but decreased almost by 3 orders of magnitude to 0.105 mg/L 10 cm away (Porter et al. 2011). Similarly, the concentration of TNT collected at the munition breach was 3.1 mg/L but decreased almost by over 2 orders of magnitude to 0.016 mg/L 1 cm away from the surface of a piece of exposed munition piece (Beck et al. 2019). Those concentrations measured right at the surface

of the exposed munition filling or piece exceeded HC₅ values. However, concentration of TNT 10 cm away from the breached item in Bahia Salinas del Sur (Porter et al. 2011) and the concentration of TNT, RDX and DNB 50 cm away from the exposed item (Beck et al. 2019) were lower than screening benchmarks.

Considering the available data on MC water column contamination and comparison of the highest concentrations for each site with available toxicity benchmarks (Table 4-4; Lotufo et al. 2017), organisms living at short distance from UWMMs are likely unaffected by MC present in the water column. However, because the concentrations of MC may be substantially higher in very close proximity to the breach on a munition (Porter et al. 2011) or centimeters away from exposed munition fragments (Beck et al. 2019) compared to concentrations at greater distances from the source (e.g., 10 cm), sessile organisms, including corals, living in those areas of localized higher MC concentrations may be adversely impacted. Similar to decreasing trends of decreasing concentrations of MC with increasing distance from the source of MC release were also reported for MC body residues of caged mussels (Maser and Strehse 2020) and in MC concentration sediment samples (Porter et al. 2004).

Table 4-4. Maximum water column concentrations of selected MC at several field sites.

Site	MC	Max Conc. (µg/L)	Toxicity Benchmark (µg/L)
Halifax Harbor (Canada) (Rodacy et al. 2001)	TNT	14.2	116
	2-ADNT	108	1,239
	4-ADNT	123	1,983
	TNB	1.24	114
	DNB	5.9	274
	2,4-DNT	3.14	43
	2,6-DNT	2.0	107
Coastal sites in Norway (Rossland et al. 2010)	TNT	0.32	116
	HMX	0.62	2,097 ³
	RDX	12.7	2,074
Bahia Salina del Sur (Vieques, PR) (Rosen et al. 2017a)	TNT	7.5	116
	2-ADNT	0.09	1,239
	4-ADNT	0.32	1,983
	TNB	0.04	114
	DNB	0.008	274
	2,4-DNT	0.07	43
	RDX	0.011	2,074
Isla de Vieques Bombing Range (Porter et al. 2011) ¹	TNT	105	116
	TNB	14.9	114
	DNB	23.4	274
	2- + 4-ADNT	107	1,239
	2-NT	54.6	NS
	RDX	4.96	2,074
Oosterschelde (van Ham et al. 2002)	TNT	0.5	116
Lake Mjøsa (Rossland et al. 2010)	TNT	0.17	116
	DNB	0.18	274
Point Amour (Canada) (Ampleman et al. 2004)	TNT	0.002	116
Lakes Thun and Brienz (Ochsenbein et al. 2008)	HMX	0.0003	2,097 ³
	RDX	0.0004	2,074
	PETN	0.0003	NS ⁴
Lakes Thun and Lucerne (Estoppey et al. 2019)	HMX	0.0003	2,097 ³
	RDX	0.0004	2,074
	PETN	0.0003	NS ⁴

Table 4-4 (continued). Maximum water column concentrations of selected MC at several field sites.

Site	MC	Max Conc. (µg/L)	Toxicity Benchmark (µg/L)
Kolberger Heide (Gledhill et al. 2019)	TNT	0.0106	116
	4-ADNT	0.000459	1,983
	2-ADNT	0.00011	1,239
	TNB	0.00027	114
	DNB	0.00946	274
	RDX	0.0019	2,074
Kolberger Heide (Beck et al. 2019) ²	TNT	50	116
	DNB	10	274
	RDX	10	2,074

¹Sample taken 10 cm from a 2000-lb bomb. Higher concentrations were reported for samples taken within the solution cavity of the bomb (see Section 3.1.1).

²Samples taken 1 to 5 cm away from the surface of a munition fragment. Dissolved TNT was 3,100 µg/L directly at the surface.

³HCS derived using no-effects concentrations

⁴NS: Toxicity data only available for fewer than six species; no calculation performed

4.2.2 Comparison of Sediment Concentrations with Toxicity Benchmarks

The HQ was calculated using ratio of the maximum concentrations of MC reported for sediment samples taken at UWMM sites and the revised sediment quality benchmarks (SQBs) presented Lotufo et al. (2017). The SQB values presented in Lotufo et al. (2017) were revisions of the preliminary SQBs for protection of benthic invertebrates developed for MC by Pascoe et al. (2010) for use in a baseline ecological risk assessment at the JPHC Superfund Site, Bremerton, WA (see Section 3.4). Pascoe et al. (2010) presented SQBs for 25 MCs as organic carbon normalized values. Organic carbon partitioning coefficients were calculated using the lowest and highest log K_{ow} available in the literature and were used to calculate corresponding SQB_{low} and SQB_{high} values.

For the studies listed below, no exceedances of revised SQBs (i.e., HQs were equal to or lower than one) were found; therefore, the potential for risks due to MC in the sediment can be considered negligible for these investigations:

- Jackson Park Housing Complex (NAVFACNW 2010c)
- Ordnance Reef 2009 sampling effort (UH2014a)
- HUMMA studies (HI-05) (Briggs et al. 2016)
- Point Amour, Canada (Ampleman et al. 2004)

Other studies reported concentrations of MC in sediment samples (Table 4-5) that exceeded screening benchmarks, indicating the potential for adverse effects to the benthic biota, as detailed below. The SQB_{low} and SQB_{high} values from Lotufo et al. (2017) are presented in Table 4-6 for MC reported in Table 4-5.

Table 4-5. Maximum concentrations (noted as 95% upper confidence limit, where indicated) of MC in sediment samples collected at UWMM sites, number of samples, number of samples exceeding benchmark, and HQs calculated using sediment benchmark values SQB_{low} and SQB_{high}. Values in bold indicate HQ>1 (rounded to the unit).

Site	MC	Conc. (mg/kg)	# of samples	# of samples exceeding SQB _{low}	HQ	
					Based on SQB _{low}	Based on SQB _{high}
Ordnance Reef UH (2014b)	2,4-DNT	6.91 ^a	56	3	2.2	0.8
	2,6-DNT	1.6 ^a	56	0	0.6	0.5
	2-NT	1.1 ^b	56	2	1.3	--
	4-TN	0.49 ^b	56	0	0.2	--
	RDX	0.14 ^b	56	1	1.5	0.9
	NG	1.7 ^b	56	0	0.6	0.2
Seattle Harbor Piers 90 and 91 USACE (2013)	2,4-DNT	0.97 ^b	12	0	0.3	0.1
	2,6-DNT	0.12 ^b	12	0	0.04	0.03
	RDX	0.058 ^b	12	0	0.6	0.4
	Tetryl	0.23 ^b	12	1	15	3
Isla de Vieques Porter et al. (2011)	TNT	506 ^{b,c}	4	4	22,200	3,608
Halifax Harbor, Canada Rodacy et al. (2001)	TNT	0.0148 ^a	23	0	0.7	0.1
	2-ADNT	0.0250 ^a	23	7	1.2	1.1
	4-ADNT	0.1185 ^a	23	1	2.5	--
	TNB	0.0080 ^a	23	5	1.3	0.6
	DNB	0.0369 ^a	23	5	3	0.9
	2,4-DNT	0.0995 ^a	23	0	0.03	0.01
	2,6-DNT	0.2111 ^a	23	0	0.1	0.1
Solstrand, Norway Rossland et al. (2010)	TNT	0.08 ^b	3	3	4	0.6
	HMX	0.06 ^b	3	0	0.4	0.1
Tælavåg, Norway Rossland et al. (2010)	TNT	0.05 ^{b,d}	1	1	2.2	0.4
	HMX	0.24 ^{b,d}	1	1	1.7	0.4
DS Selma, Norway Rossland et al. (2010)	TNT	0.31 ^b	2	2	14	2.2
	HMX	0.41 ^b	2	2	4	3

*a: 95% upper confidence limit; b: maximum concentration or single sample; c: sample taken 0.1m distance from bomb; d: sample taken before detonation.

Table 4-6. Sediment quality benchmarks (SQB) for MC (from Lotufo et al. 2017).

MC	Selected toxicity value (Pascoe et al. 2010)	Selected K _{oc} (Pascoe et al. 2010)		SQB at 1% OC (Pascoe et al. 2010)		Revised SQB (1% OC and 70% solids)	
		low	high	low	high	low	high
	µg/L			mg/kg		mg/kg	
TNT	28.4	37.4	451	0.011	0.128	0.023	0.140
2-ADNT	19	65.9	81	0.013	0.015	0.021	0.024
4-ADNT	30	116	no data	0.036	--	0.048	-
2,4-DNT	2400	88.4	300	2.1	7.2	3.2	8.2
2,6-DNT	1800	116	150	2.1	2.7	2.9	3.5
2-NT	3400	182	no data	6.2	--	7.6	-
4-NT	320	214	no data	0.68	--	0.82	-
DNB	17	29.2	210	0.005	0.036	0.012	0.043
TNB	11	14.5	77	0.0016	0.0086	0.0063	0.0132
Tetryl	15	41.9	406	0.006	0.061	0.013	0.089
HMX	330	1.15	130	0.0038	0.43	0.1452	0.6
RDX	186	6.26	42	0.012	0.078	0.091	0.2
NG	3230	39.2	180	1.266	5.814	2.65	7.20

Ordnance Reef 2012 FUI (UH2014b)

The HQ values calculated using the 95% UCL or maximum concentration were 1 or less (rounded to the nearest unit) for 2,6-DNT, 2-NT, 4-NT and NG. Only one out of 56 samples from the munitions disposal site had detectable concentrations (0.14 mg/kg) of RDX. That concentration exceeded the SQB_{low} (0.091 mg/kg, Table 4-5) by a factor of 1.5 but was lower than the SQB_{high}. Considering the detection limit for RDX reported for that study, all other 55 samples had MC concentrations lower than the SQB_{low}. Therefore, potential for risks from exposure to RDX in the sediment can be considered negligible when considering the concentration distribution at the site. The HQ for 2,4-DNT, detected in 31 out of 56 samples (55%) in the DMM stratum, derived using the 95% UCL sediment concentration (6.91 mg/kg) was 2.2 using the SQB_{low}, but was 0.8 using the SQB_{high}. Therefore, the potential for adverse effects of 2,4-DNT to benthic organisms is possible based on the comparison of the 95% UCL sediment concentration with the SQB_{low} value.

Former Seattle Naval Supply Piers 90 and 91 (USACE 2013)

Four MC (2,4-DNT, 2,6-DNT, RDX and tetryl) were detected in up to 3 samples out of 12. The nitroaromatic MC 2,4-DNT, 2,6-DNT and RDX were detected at concentrations lower than the revised SQB for those MC; therefore, the potential for risks can be considered negligible. Tetryl was detected in one sample out of 12 at a concentration (0.23 mg/kg) that exceeded the revised

SQB for this MC. Because the limit of detection (LOD) for tetryl (0.06 mg/kg) exceeded the revised SQB_{low} for that MC (Table 4-6), uncertainty remains regarding the risk posed by tetryl to benthic invertebrates for the site. The LOD was also higher than SQB values for TNT, 2-ADNT, 4-ADNT, DNB, TNB, 3,5-DNA, and HMX. Therefore, even though these MC were not detected in any samples, uncertainty remains regarding the risk of these MC to benthic invertebrates. In conclusion, the potential for toxicity to benthic invertebrates from exposure to MC in sediment from the former Seattle Naval Supply Piers 90 and 91 cannot be ruled out. Uncertainty associated with this screening-level evaluation exists in part because of analytical challenges associated with achieving LOD required for comparisons with SQB values, as noted by Pascoe et al. (2010). Moreover, the provisional nature of the SQB values presented in Pascoe et al. (2010) and revised SQBs derived by Lotufo et al. (2017) remains.

Halifax Harbor (Rodacy et al. 2001)

The HQ values calculated using the 95% UCL for MC in sediment samples were 1 or less (rounded to the unit; i.e., 0.7, 1.2 and 1.3 are rounded to 1) for TNT, 2-ADNT, 1,3,4-TNB, 2,4-DNT, and 2,6-DNT. The HQ for 4-ADNT, detected in 39% of the samples, was 2.5 using the revised SQB_{low}. The HQ for DNB, detected in 22% of the samples, was 3 using the revised SQB_{low}. Those exceedances indicate the potential for adverse effects. However, a revision of the SQB values for 4-ADNT and DNB using chronic Water Quality Criteria derived by Lotufo et al. (2017), instead of benchmark values used by Pascoe et al. (2010) would result in revised SQBs higher than the 95% UCL concentrations for these MC and, therefore, would indicate a negligible potential for risk, as detailed in Lotufo et al. (2017). Because of the provisional nature of the SQB values presented in Pascoe et al. (2010) and revised SQBs derived by Lotufo et al. (2017), uncertainty remains.

Coastal Fortifications in Norway

The concentrations of TNT and HMX in sediment samples taken in the proximity of UWMM at coastal fortifications in Norway (Rossland et al. 2010) exceeded revised SQB_{low} by factors ranging from 2 to 14 (TNT) and 2 to 4 (HMX) in most locations. Based on spiked sediment studies that reported the lack of effects at the highest concentration tested (115 to 353 mg/kg; Lotufo et al. 2001, Steevens et al. 2002), the maximum concentration of HMX reported across sites (0.41 mg/kg) was not expected to be associated with acute and sublethal effects to the benthos. Likewise, based on spiked sediment studies that reported NOEC values for TNT ranging from 20 to 275 mg/kg for marine amphipods and polychaetas (Green et al. 1999; Lotufo et al. 2001; Rosen and Lotufo 2005), the maximum concentration of TNT reported across sites (0.31 mg/kg) was also not expected to be associated with acute and sublethal effects to the benthos. The concentrations for other MCs were reported as either “trace” or below DL across sites. Because the LOD was not provided for most MC analyzed and scarcity of data derived from spiked

sediment toxicity tests, uncertainty remains regarding the risk posed by additional MCs at this site.

4.2.3 Conclusions regarding risk posed by MC in sediment

Exceedances of MC concentrations in sediment relative to revised SQB values occurred in seven UWMM sites (Table 4-5). For sites where a relatively large number of samples were taken and for which the sampling effort was aimed at the characterization of the entire impacted area (HI-06, former Seattle Naval Supply Piers 90 and 91, and Halifax Harbor), MC-specific exceedances of SQB values were limited to a small portion of the samples (12% of the samples or less). Therefore, based on a conservative screening-level evaluation (Pascoe et al. 2010), the potential for risk to benthic invertebrates is limited to only a small portion of the site. However, risk from exposure to MC that may be present in sediment at the former Seattle Naval Supply Piers 90 and 91 cannot be ruled out because the LOD (USACE 2013) was lower than their respective revised SQBs.

The other sites listed in Table 4-5 were subjected to a limited assessment concerning contamination of MC in sediment surrounding one or several UWMM (concentrated in a small area). Potential for risk was identified at targeted sampling areas in coastal Norway (Rossland et al. 2010) and Puerto Rico (Porter et al. 2011), but the lack of sampling beyond the targeted area prevented assessing risk to the benthic community inhabiting those UWMM sites.

4.2.4 Evaluation of Risk Using MC Concentration in Biota

Studies of the lethal effects of MC have reported whole-body tissue concentrations (or whole-body burden) of test organisms sampled at termination of the exposure period used to generate toxicity data (Rosen and Lotufo 2007a; Lotufo et al. 2010; Lotufo et al. 2013). Available critical residues associated with mortality of organisms exposed to MC are reported in Lotufo et al. (2013) as median lethal residues. In the case of exposures that did not result in mortality, they are reported as the no observed effect residue, which are body residues in organisms surviving the highest exposure concentrations.

When the whole-body residue can be linked to a specific biological effect, the body residue is termed the critical body residue (McCarty and Mackay 1993). Tissue residue concentrations may be more directly relatable to toxic effects than water-based concentrations and provide an integrated assessment of the exposure an organism receives over time and space (Meador 2006). However, given that body burdens can rapidly depurate or metabolize, preventing tissue concentrations from persisting at levels that may cause detrimental biological effects, the elimination rates for MC has been reported as very rapid (Rosen and Lotufo 2007b; Lotufo et al. 2013, 2016). Fish and invertebrates inhabiting UWMM areas are expected to experience harmful effects only if under fairly constant exposure conditions.

MC have a low propensity to bioaccumulate in fish and invertebrates via exposure to water and sediment (Lotufo et al. 2009a; 2013; 2016, Ballentine et al. 2015, 2016; Voie and Mariussen 2018). The low bioaccumulation potential of MCs joined with their propensity to rapidly disappear from exposed organisms following a decrease of MCs in the water column diminishes the relevance of using body residue in biota for assessing risks to fish and invertebrates inhabiting UWMM sites. The use of biota contamination data is further complicated by the paucity of tissue-based toxicity metrics used to assess the proper selection of toxicity reference values for assessing risk of MC. For the above reasons, an attempt to evaluate risk at UWMM sites using available biota data has not been made.

4.3 Underwater Munitions Constituents Vieques Naval Training Range (Puerto Rico)

4.3.1 Background

From the mid-1940s until 2003, the Vieques Naval Training Range served as the Navy's premier training range for ensuring combat readiness of U.S. Atlantic Fleet and Allied forces. During this time, more than 300,000 munitions were dropped or fired during military training operations, including naval gunfire, air-to-ground bombing, and marine artillery fire. Currently, the underwater areas associated with the former Vieques Naval Training Range comprise 12,000 acres potentially impacted by munitions lying on or beneath the ocean floor.

4.3.2 Research

Several investigations have been conducted at Vieques to characterize the impact of MC in underwater areas containing munitions or receiving runoff from nearby terrestrial munitions sites.

In 2005, the National Oceanic and Atmospheric Administration (NOAA) conducted a study of MC effects on fiddler crabs and land crabs. The study found no explosive compounds or other contaminants at levels potentially harmful to human health. Within the former Live Impact Area (LIA), the concentrations of arsenic, cadmium, and selenium were elevated above reference locations on the main island of Puerto Rico; however, munitions contain very little, if any, of these inorganics, indicating that munitions were not the source of the elevated levels. Based on the findings of the NOAA study, the Agency for Toxic Substances and Disease Registry (ATSDR) determined that there was no human health risk from eating land crabs on Vieques (ATSDR 2003, 2006, 2013).

Between 2006 and 2010, NOAA conducted an ecological characterization of marine resources of Vieques. As part of the study, NOAA collected sediment samples in offshore areas and inland lagoons that were known to contain munitions or receive runoff from terrestrial munitions sites.

No explosive compounds were detected in any of the samples (NOAA and Ridolfi 2006; Pait et al. 2010).

In 2013, the Navy initiated a remedial investigation (RI) in the former LIA, which includes a 20-acre lagoon (Laguna Anones) that was heavily impacted by munitions. Given its location, Laguna Anones was expected to have the highest concentrations of MC in and around Vieques. However, the results of the RI showed no detections of explosives in water or sediment, and inorganics concentrations were consistent with background/reference locations (CH2MHill 2015).

In 2014, NOAA conducted an independent evaluation of MC in fish, lobster, and conch around Vieques. The researchers were unable to catch any fish, but lobster and conch showed no detectable explosive compounds, and concentrations of inorganics were consistent with background/reference concentrations (Whitall et al. 2016).

In 2015, the Space and Naval Warfare (SPAWAR) Systems Center Pacific (now Naval Information Warfare Center (NIWC) Pacific) conducted a MC investigation of surface water, sediment, and porewater in a Vieques bay with high densities of underwater munitions. The investigation included the use of passive sampling devices deployed in a grid pattern, along with additional samplers placed adjacent to potentially breached munitions. In the sediment and porewater samples, all explosives were non-detect. In surface water, TNT was detected at 5.3 µg/L at one location approximately 12 inches from a breached 1,000 lb bomb. For all other locations, most explosives were non-detect, and the few detections were in the low ng/L range (Rosen et al. 2017a). Most importantly, all MC concentrations were substantially lower than the levels determined to be harmful to the most sensitive aquatic species and ecotoxicological endpoints. In addition to this work on Vieques, passive samplers were used to measure underwater MC at a field research station in Gulf Breeze, Florida. Samplers were deployed at varying distances from 15 g of Composition B (59.5% RDX, 39.5% TNT, 1% wax) that was directly exposed underwater (Rosen et al. 2018). Ultralow MC detections (low ng/L range) were observed 2 meters from the exposed explosives, but there were no detections at 5 meters. All of the detected MC concentrations were substantially lower than the levels determined to be harmful to the most sensitive aquatic species. Taken in context with other research and investigations at Vieques or elsewhere (e.g., Beck et al. 2019), the Gulf Breeze study eliminates the concern that these kinds of underwater munitions are “ticking time bombs” that will ultimately release large amounts of conventional MC when the casings breach.

4.3.3 Results/Lessons Learned

The studies at Vieques and Gulf Breeze are consistent with other research efforts that show MC related to underwater munitions as appearing to have limited adverse impacts on surface water and sediment quality, and aquatic species. In all cases, MC was detected only within a few feet of the explosive material, and beyond this narrow range, the results were below detection limits

(i.e., low ng/L concentrations). In addition, detected MC concentrations were always substantially lower than levels determined to be harmful to the most sensitive aquatic species based on the limited toxicity studies available. Therefore, underwater munitions do not act as a “pinpoints of contamination”, leaving the vast majority of the underwater area completely unaffected. In the context of a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) human health or ecological risk assessment, these small “points” of MC contamination would not produce unacceptable risk because exposure to these localized areas would be insignificant compared to the larger exposure areas of human underwater activity, the home range of motile aquatic organisms, or populations of sedentary organisms. However, in the context of Endangered Species Act (ESA) consultation, for example, potential biological impacts to a single organism or colony (e.g., corals) of a species listed as threatened or endangered under ESA, is considered an adverse effect. Therefore, it is important to consider the aspect of scale differently for ESA-listed species compared to biota that are not listed.

Results of the studies mentioned above, and related studies should be clearly communicated to the public to increase their knowledge and minimize concerns. Without proper communication, the public will continue to have unwarranted concerns about MC that are based on misunderstandings of how munitions and MC actually behave underwater. Regulatory agencies, natural resources agencies, and the lead DoD agencies can move projects forward by emphasizing the results of current research on underwater MC. Proper communication will help stakeholders understand the MC issue and focus on more significant impacts to the underwater ecosystem (for example, overfishing of spawning areas and temperature effects on coral).

Overall, the existing science of underwater MC supports a conceptual site model (CSM) in which MC is localized around individual munitions items and otherwise below the limit of analytical detection. These localized areas are so small that human health and ecological risk assessments are unlikely to identify MC compounds as contaminants of concern. However, if a risk assessment is focused on ESA-listed species, the risk could be considered significant. This general CSM will apply to most, and perhaps all, underwater munitions sites associated with former military ranges as well as disposal sites and shipwrecks. Therefore, the nature and extent of MC at underwater munitions sites can be adequately determined from the current state of scientific knowledge, without the need for additional sampling. Rather than continuing to sample and analyze for underwater MC, project teams should focus limited resources on other, more significant issues such as identifying and removing explosive hazards.

4.4 Remedial Action Decision Making for the Navy Jackson Park Underwater Munitions Site

This section provides an overview of the RI and cleanup activities to date at the Jackson Park Housing Complex (JPHC)/Naval Hospital Bremerton (NHB) Superfund site in Kitsap County, Washington. The site was placed on the USEPA National Priorities List in 1994 due to past disposal

activities by the Navy from use of the facility as Naval Ammunition Depot (NAD) Puget Sound from 1904 to 1959. The primary activities by the Navy during this time period include Load Assemble and Pack, transfer, storage, and demilitarization of U.S. Navy munitions, particularly during WW II. As of a second 5-year NAVFAC review of the site published in 2011, it remained unclear as to the risks of DMM on human health from shellfish (NAVFAC NW 2011).

Underwater munitions are present at the site from loss and mishandling of ordnance during pier side loading operations on adjacent Ostrich Bay shown in Figure 4-1. After NAD Puget Sound was closed, the site was redeveloped in the 1970's as a Naval housing complex and hospital, and adjacent properties were transferred for use as highways, municipal parks, and housing complexes. The area in general is heavily encroached by residential housing.

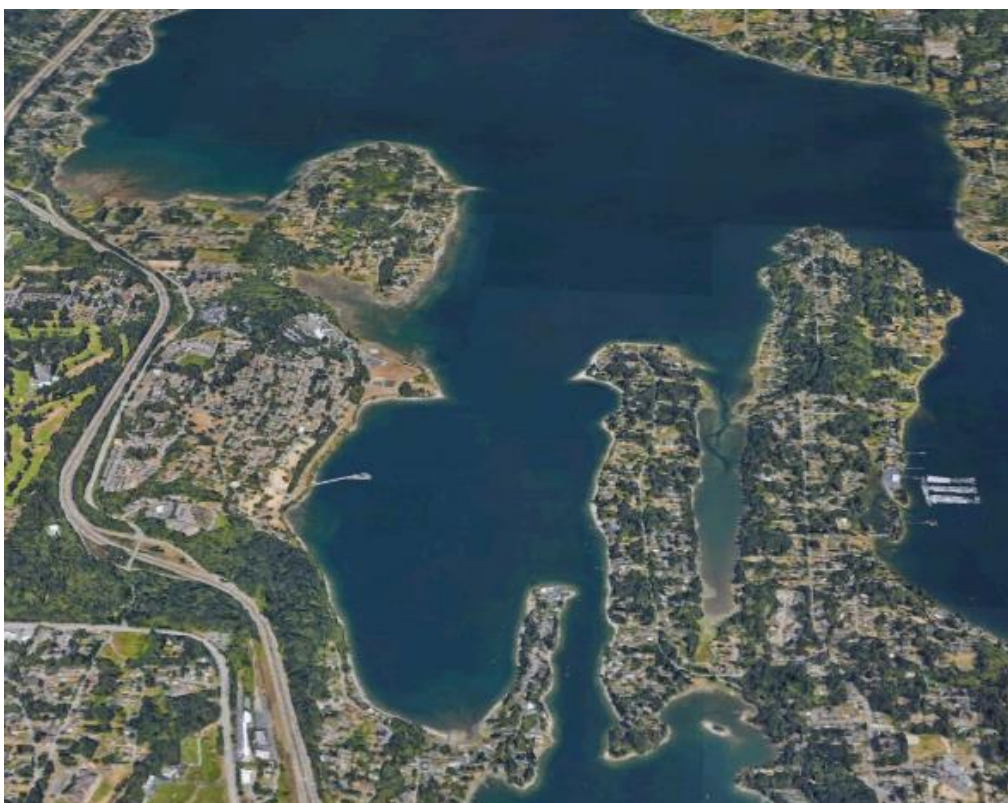


Figure 4-1. Ostrich Bay, WA – Current Jackson Park Housing Complex (JPHC) on the left side.

In 2004, NAVFAC Northwest and USEPA Region 10 signed a two-party Federal Facilities Agreement (FFA) that covers the legal and procedural process for investigation and remediation of contamination at the site, including upland and underwater munitions. The Suquamish Tribe has Tribal treaty rights in Ostrich Bay for fisheries based on Usual and Accustomed gathering areas. The Tribes in the Puget Sound region jointly manage fisheries with the State of Washington.

During the operation of NAD Puget Sound, a number of buildings existed on the western shoreline of Ostrich Bay for storage and refit of U.S. Navy munitions. Demilitarization activities resulted in discharge of explosives contaminated wastewater into Ostrich Bay, primarily after WW II. Loading and unloading of munitions occurred at three locations, Pier 1, Pier 2, and the Railroad Handling Pier. Moorings and dolphin pilings also existed for the purposes of staging lightering barges for loading and unloading operations (Figure 4-2).

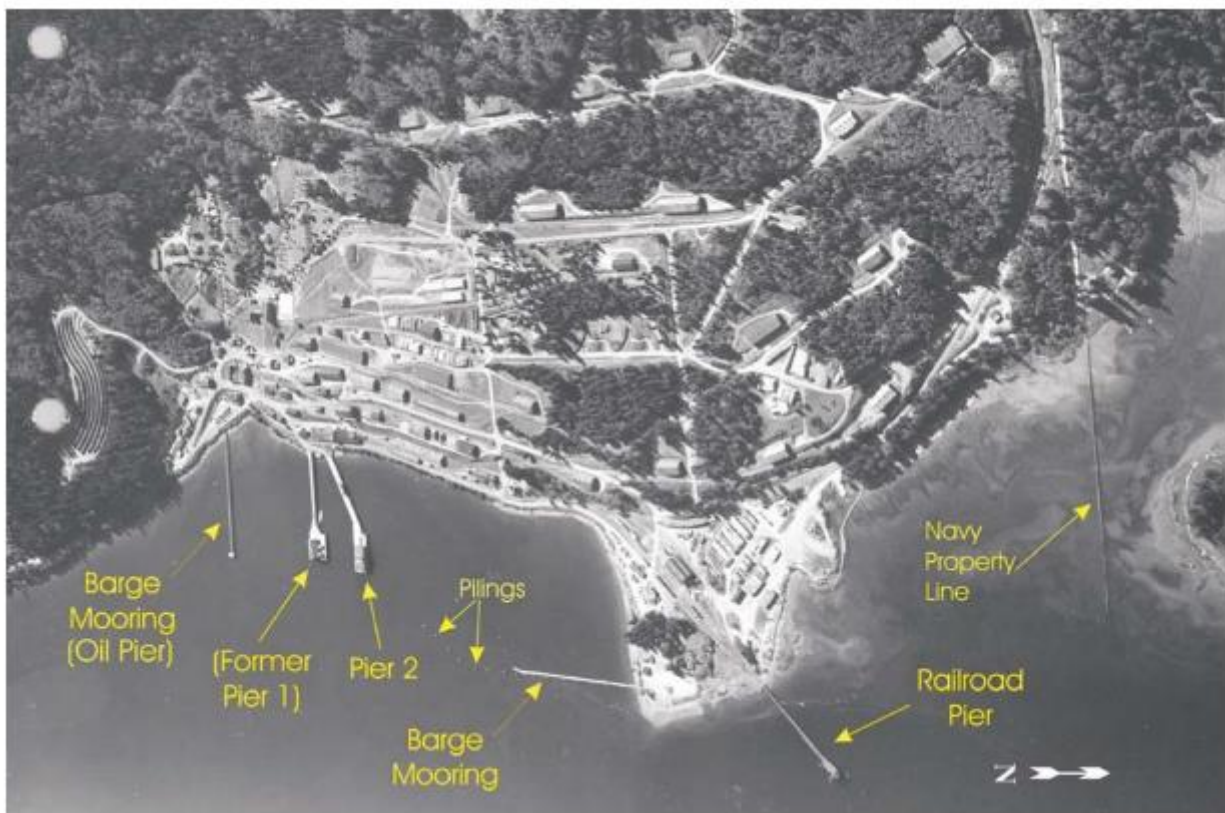


Figure 4-2. Former Naval Ammunition Depot (NAD) Puget Sound, circa 1959.

After NAD Puget Sound was closed and redeveloped as a housing complex and hospital, most of original structures were demolished and replaced with Navy housing, community structures, and NHB. Under the CERCLA FFA, the site inspection for munitions was divided into three munitions operable units (OUs), 1) JPHC, 2) NHB, and 3) Ostrich Bay. The JPHC OU included the intertidal areas of the site, which has a diurnal 12-foot tidal range. Pier structures were also demolished, with only Pier 2 currently remaining.

The original underwater investigation of the Ostrich Bay OU in 2004 included a high resolution multibeam bathymetric (MBB) survey to identify the depths, contours, and potential obstacles for follow-on marine magnetometer surveys for underwater munitions. The MBB survey identified previously unknown dredge cuts around Pier 2, despite an extensive diver survey for surface munitions around the piers in 1981. The MBB survey did not identify dredge cuts around

former Pier 1. Further records research identified that the Pier 2 dredging occurred sometime during WW II, the dredging did not exist in 1941 and did in 1945.

The initial marine magnetometer survey was conducted in 2008 to test the performance of a towed-array “flown” system (SAIC Marine Towed-Array) initially developed under an ESTCP project (Figure 4-3). An underwater Geophysical Prove-Out was conducted prior to the semi-production survey to establish the performance of the systems for detection of typical WW II era Navy munitions. The initial marine magnetometer survey in 2008 comprised approximately 60% of Ostrich Bay, with identified geophysical anomalies. A follow- on survey completed the marine magnetometer survey of the entire bay using the same instrumentation and post-processing.



Figure 4-3. Geophysical Prove-Out of Marine Magnetometer Survey, Ostrich Bay, WA. A pontoon boat towed the sensor platform, which is submerged 7 ft below the surface.

Based on the full marine geophysical survey, approximately 1100 anomalies were identified in Ostrich Bay. Diver investigation of detected magnetic anomalies identified approximately 300 munitions items in Ostrich Bay shown in the locations in red (Figure 4-4). The histogram of recovered depths of munitions items is shown in Figure 4-4. Smaller munitions items (e.g., 40 mm projectiles) were recovered at shallower depths (~ 6 to 12 inches), whereas larger munitions items (e.g., 5 and 6-inch projectiles) were recovered at deeper depths (~ 36 inches). Ostrich Bay is a net depositional environment in a majority of the bay with sediment deposition rates of 0.2 to 0.8 cm/year.

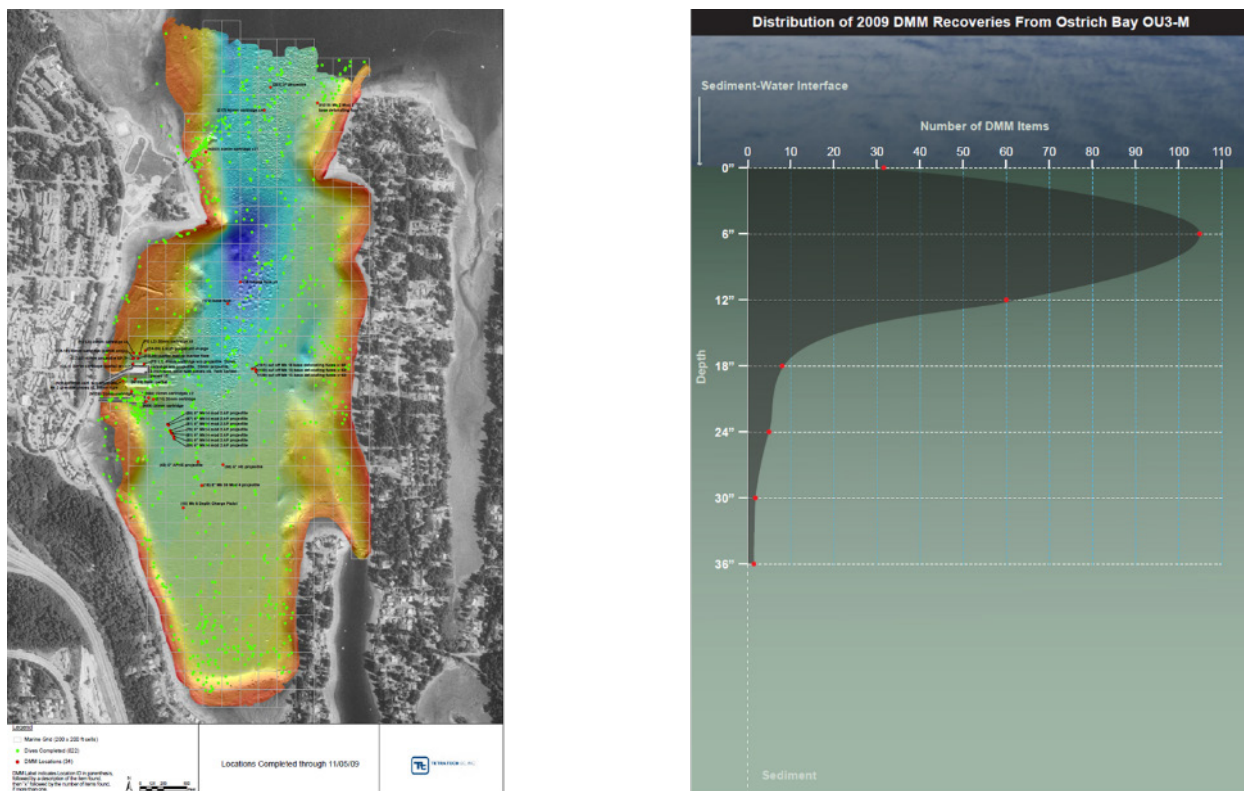


Figure 4-4. Spatial (left) and vertical (right) locations of Recovered DMM in Ostrich Bay.

Recovered munitions from Ostrich Bay include a range of typical WW II and earlier munitions items. Items recovered in deeper parts of the bay tended to have less corrosion and some degree of mud/concretia on the munitions items. Smaller munitions items recovered in the intertidal and shallow subtidal areas had greater corrosion and less concretia formation on the munitions items (Figure 4-5).



Figure 4-5. Typical condition of recovered DMM by divers in Ostrich Bay, WA.

The range of potential organic munitions compounds at this site include nitroaromatics (TNT, DNTs) nitramines (RDX, HMX) nitrate esters (NG, PETN), and nitrophenols (ammonium picrate/picric acid) used as secondary explosives and gun propellants in munitions. Metals present include mercury and lead from use as primary explosives in primers, fuses, and detonators.

Benthic bioassay studies conducted showed unresolved toxicity at a number of stations in Ostrich Bay based on standard benthic toxicity screening tests (Carr et al. 2001). As a result, additional studies were conducted (Carr and Nipper 2003, Nipper et al. 2001, 2002, 2004, 2005) to further elucidate the potential causes of sediment toxicity, and to develop a better understanding of the toxicity of environmental transformation products of MC in marine environments, for which there was limited data in the literature. A second phase of ecological toxicity testing was conducted in 2009 based on multiple lines of evidence including 1) benthic sediment chemistry, 2) benthic bioassays at corresponding locations, and 3) marine tissue sampling of relevant ecological receptors (clams, crabs, benthic fish, etc.). The remedy decisions on ecological risks at the site were based on all three lines of evidence.

The technical approach for a 2009 site-specific ecological risk assessment was based on standardized USEPA analytical methods for explosives and metals for sediment analysis, and specifically developed analytical methods for explosives in marine tissue samples, as summarized below.

- Sediment chemistry - surface and core samples
 - 0-10, 10-50, 50-90 cm cores, 0-10 cm grab samples used for whole sediment bioassays
- Analytes – energetics, metals, semivolatile organic compounds
 - SW-846 Methods 8330B, 6010, 8270 for sediments
- Whole sediment bioassays
 - WA Department of Ecology Protocols – Four acute and chronic toxicity tests
- Tissue sampling – five species (clams, geoducks, sea cucumbers, Dungeness crab, and starry flounder)
 - Site-specific developed HPLC-UV and HPLC-MS tissue methods

Diver reconnaissance surveys were conducted in 2008 based on transects to identify the most abundant and representative species for evaluation. Ecological receptors were prioritized based on commercial and Tribally relevant species, particularly focusing on detritus feeders, filter feeders, and benthic fish most likely to be exposed to contaminants in sediments. Based on the results of the site-specific ecological risk assessment, slightly elevated risks were shown for higher trophic organisms for selected metals. Based on these results, and the improvement in

the results of the benthic bioassays from 2000 to 2009, Monitored Natural Recovery (MNR) was selected as the preferred remedial alternative for the site.

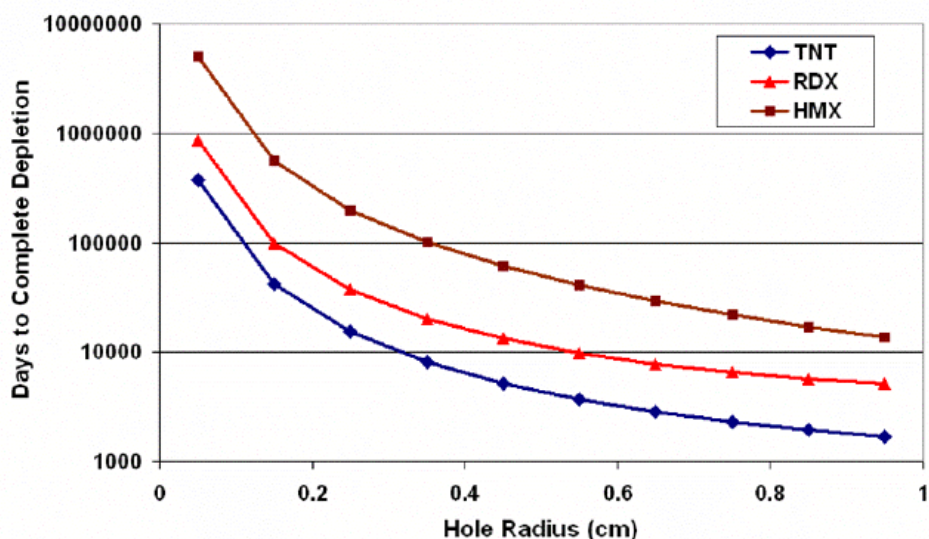
For the purposes of human health risk assessment for Ostrich Bay, marine tissue monitoring has been conducted since the OU-1 Record of Decision in 2000. Over the past 14 years, there have been sporadic detections of nitroaromatics and nitramine compounds in clam and crab samples, but no consistent trends (Table 4-7). A number of data quality challenges occurred during this time period, including no matrix specific detection limit studies for MC in tissues prior to 2009. In addition, no analysis of nitrophenols (picric acid, picramic acid, etc.) in tissue samples were conducted prior to 2009. Analysis of MC in marine tissue samples is inherently difficult due to potential matrix interferences, and the relatively polar nature of energetic MC.

Table 4-7. Time series munitions compounds detected in marine biota, Ostrich Bay, WA

Sampling Year	Organism	Chemical	Number Detected/Number Sampled	Range of Detections (mg/kg)	Suquamish Shellfish Screening Level (mg/kg)
2002	Site Clam	4-ADNT	6/15	0.13 – 0.28	0.33
		RDX	2/15	0.13 – 0.46	0.0035
	Reference Area Clam	4-ADNT	1/3	0.12	0.33
	Site Crab	TNB	1/10	0.083	4.96
2004	Site Clam	RDX	3/15	0.18 – 0.28	0.0035
2009	Site Clam	2,4-DNT	3/15	0.047 – 0.053	0.0012
		2,6-DNT	2/15	0.077; 0.13	0.165
	Reference Area Crab	Tetryl	1/3	0.086	0.66
2014	Site Clam	2-NT	2/15	0.035; 0.49	0.0017

Corrosion and electrolysis of munitions casings in seawater is expected to occur for those disposed of in the ocean, even in northern climates. Modeling of MC dissolution out of the casings has a large degree of uncertainty. Figure 4-6 shows the approximate dissolution timeframe for a 1 cm hole (25 years) and a 1 mm hole (2,700 years) for RDX in a Composition B (TNT/RDX) filled 8-inch projectile, estimated using the Shell Model (Wang et al. 2013).

TNT-RDX-HMX
(Shell: L=24", D=8", 8kg)



Release time for TNT, RDX, and HMX under the same conditions ($U = 15 \text{ cm/s}$).

Figure 4-6. Dissolution timeframe estimated for an 8" munition using the Shell Model (Wang et al. 2013).

Remedial action decision making for underwater munitions and MC at the JPHC/NHB site is based on three remedial decisions: 1) OU-3M - underwater DMM (source material and safety risks), 2) OU-1 - human health risks (cancer and non-cancer) from ingestion of contaminated marine tissues, 3) OU-2 – ecological risk to higher trophic level receptors from ingestion of prey species.

For OU-3M, approximately 300 munitions items have already been removed from Ostrich Bay, and the remaining area of concern (AOC) is the 10-acre area around Pier 2, the most heavily used area of the site. Dredging and diver removal of munitions will occur within the 10-acre area for the remaining detected subsurface anomalies. For OU-1, continued monitoring will occur until tissue samples show acceptable cancer and non-cancer risks for subsistence consumption scenarios for the Suquamish Tribe in Ostrich Bay. For OU-2, continued monitoring will occur for mercury in tissue samples to demonstrate a stable or downward trend in tissue concentrations to ecological receptors. For the AOC around Pier 2, 3220 anomalies remain in the 10-acre area. The selected remedy for OU-3M includes dredging and diver removal of remaining anomalies, and geophysical verification of removal of these subsurface anomalies.

Commercial and Tribal geoduck harvesting in Puget Sound include use of water “lances” to liquefy sediment up to a depth of 3 feet below the sediment/water interface to recover geoducks. The depth of subsurface clearance of military munitions around Pier 2 is based on this potential depth

of intrusive use in the future. Sea cucumber harvesting in Puget Sound is conducted commercially by divers with umbilical air lines to the boat. Sea cucumber harvesting is primarily a surficial activity at the sediment/water interface.

Lessons learned based on 15 years of experience of multiple geophysical, bioassay, and chemical sampling investigations at the JPHC/NHB site are:

- Ensure bathymetric and underwater geophysical surveys are comprehensive;
- Phase/design MC chemical sampling based on the results of geophysical surveys;
- Tissue sampling for assessing both human health and ecological risks can be accomplished in a single sampling event provided adequate planning is conducted to accomplish both objectives;
- Tissue sampling and analysis for MC is not trivial and should be carefully evaluated based on the commercial laboratories demonstrated performance specifically on tissue samples; and
- Multiple lines of evidence are necessary for decision making purposes, no data set is perfect for all uses.

4.4.1 Conclusions

While modeling provides a preliminary framework for site investigations, it does not substitute for site-specific data on which to evaluate explosive safety, human health, and ecological risks from munitions in the underwater environment. For some components such as dissolution kinetics of MC, almost no data exists for real world site conditions, and current modeling efforts cannot quantitatively account for the full range of variables that may exist in the underwater environment, including casing corrosion, concretia, dissolution kinetics of specific explosive fillers, temperature effects, equilibrium partitioning, chemical transformation, and munitions movement due to weather events.

The public is rarely satisfied with modeling risks to human and ecological receptors without site-specific data used to verify that modeling assumptions are valid and accurately predict environmental conditions. Public confidence in remedial decision making comes from comprehensive site-specific data used in a transparent manner to assess the risks and uncertainties at a specific site.

4.5 *Investigating and Monitoring Sea-disposed Munitions at Deep Water Sites Near Oahu, Hawaii*

Sea disposal was once internationally accepted as an appropriate method for disposal of excess, obsolete, and unserviceable conventional and chemical munitions. The U.S. DoD ceased this practice in 1970 and the Marine Protection, Research and Sanctuaries Act of 1972, also known

as the Ocean Dumping Act, prohibited disposal without a permit; no permits have been issued to DoD (Section 1.2 of this report). The past decade has seen an increase in the number and complexity of studies to assess the effects of historical munitions disposal in the oceans. HUMMA was established by the DoD in 2007 to investigate the region south of Pearl Harbor, Oahu, Hawaii (<http://www.hummaproject.com/>). Historical documents indicated that approximately 16,000 M47A2 100-lb mustard-filled bombs were disposed in the area between October and November of 1944. These boundaries of sea disposal site, designated HI-05 by the DoD were poorly defined and overlapped with another disposal site in the same general vicinity, designated HI-02. Historical documentation for HI-05 only identifies chemical DMM at the site but HI-02 documentation shows disposal of both chemical and conventional munitions, providing the opportunity to investigate the environmental effects of different types of MC (UH and Environet 2016; DoD 2010) ⁵. This region, which stretches from Barber's Point on the western side of the Oahu to Diamond Head crater on the eastern side and from Pearl Harbor to 50 km due south of Oahu, was selected for the HUMMA study. The northern boundary of the study area contains a shallow shelf (water depths ranging from 50 to 75 m) that extends south for approximately 3.2 km. South of the 3.2-km mark there is an abrupt drop-off to ~300 m depth (Figure 4-7). Temperatures typically range from 6 to 8 °C (UH and Environet 2010) (Edwards et al. 2016a).

⁵ Department of Defense 2010. Defense Environmental Programs, Annual Report to Congress, Fiscal Year 2009, Chapter 10 Sea Disposal of Military Munitions. April.

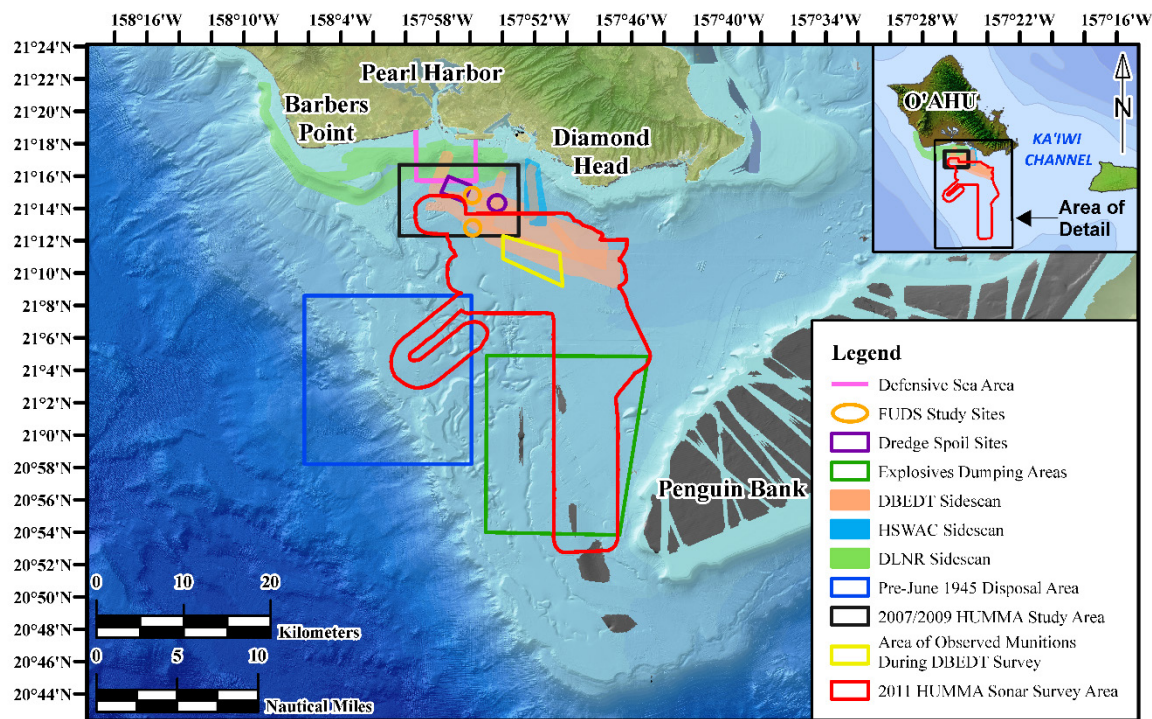


Figure 4-7. HUMMA survey areas (UH and Environet 2016).

Notes: Color-coded, shaded relief bathymetry for the region south of Pearl Harbor on the Island of O’ahu, Hawai’i. The locations of important sites (i.e., historic dredge spoil and munitions dumpsites) and the various SONAR datasets that were compiled into the HUMMA Geographic Information System (GIS) are shown. The legend indicates dataset and boundary colors. HSWAC - Honolulu Seawater Air Conditioning

HUMMA’s focus was to the partial fulfilment of the research requirement of Public Law 109-364 § 314 to address some of the requirements “to conduct research on the effects on the ocean environment and those who use it of military munitions disposed of in coastal waters.” This includes “determine whether the disposed military munitions have caused or are causing contamination of such waters or sea beds” and the “investigation into the long-term effects of seawater exposure on disposed military munitions, particularly effects on chemical munitions”, and the “investigation into the impacts any such contamination may have on the ocean environment and those who use it, including public health risks.”⁶

⁶ U.S. Congress 2006. Public Law 109-364, Section 314. Research on Effects of Ocean Disposal of Munitions. October 17.

The initial HUMMA effort was a side-scan Sonar (SSS) investigation of the study area in August 2007. The purpose of this investigation completing a wide-area reconnaissance survey of the area south of Pearl Harbor to compile an inventory of foreign objects on the seafloor. Data analysis suggested that thousands of man-made objects were detected, including several scatter fields of multiple munitions objects within the survey area (Edwards et al. 2012).

To achieve the objectives of the Public Law, the 2009 and 2012 field programs (UH and Environet 2010; Edwards et al. 2012; Edwards et al. 2016a; Carton et al. 2014; UH and Environet 2016) sampled sediment at chemical and conventional DMM at depths of 400–650 m to quantify the distribution of chemical agent (CA), energetics, and select metals in proximity to sea-disposed munitions and compared these results to nearby control sites. Additionally, HUMMA had technological objectives to develop and demonstrate effective, cost-efficient methodologies for surveying and sampling other historic munitions sea disposal sites.

In March 2009, the HUMMA project team revisited the area with underwater ROVs and deep-sea HOVs to identify the disposal sites and to confirm the presence of DMM. Munitions encountered confirmed that munitions were disposed over the side of vessels as they steamed forward. Munitions encountered during this investigation were visually assessed for casing integrity. Records were sent to experts for munitions type identification. Water and seafloor sediment samples were collected in the vicinity of the identified disposal sites and at control sites away from the identified disposal sites. Samples were analyzed aboard ship and shipped to mainland laboratories for analysis for explosives and chemical agents and their breakdown products to assess the potential impact of the undersea munitions on human health and the environment.

From April through May 2009, a separate field effort was launched to collect human food item biota samples in or near the HUMMA Study Area took place and from where the submersibles collected water and seafloor sediment samples. The two targeted food items likely to be consumed by humans that were sampled were a highly prized finfish *Etelis coruscan* (known locally as onaga) and a commonly eaten shrimp *Heterocarpus laevigatus* (ama ebi) (Koide et al. 2016). Samples were caught using the same methods that commercial and recreational fishermen use (e.g., rod and reel for fish, traps for shrimp). These samples were observed for deformities, eroded fins, lesions, and tumors, as well as prepared, and sent to the mainland for chemical agents, energetics, and metals analysis. Although the 2009 HUMMA survey successfully identified more than 2,500 munitions and collected samples near 20 munitions, no 100-pound mustard bombs were identified (Carton et al. 2014).

The 2012 HUMMA field effort used HOVs to collect 212 samples (153 sediment, 36 shrimp, 12 in fauna, six deep-sea dwelling starfish and five water) within 6 feet of 100-pound mustard bombs and at control sites (Carton et al. 2014; UH and Environet 2016). An innovative mass

spectrometer was deployed on three HOV dives to collect *in situ*, real-time readings for chemical agent in seawater at select munitions sites, with results correlated against the discrete samples collected for laboratory analysis. Additionally, 30,000 high-definition downward-looking photographs were collected during 17 transects through the area, two time-lapse cameras were deployed to observe the interactions of marine life with munitions, and shrimp and starfish in direct contact with munitions were collected (Edwards et al. 2016b); the latter action resulted in the discovery of a new starfish species (Mah 2016).

In 2014, Woods Hole's ROV JASON 2 was used. Two time-lapse digital still cameras were deployed near munitions during the 2012 HUMMA program to observe faunal behavior over periods of one to three days. One of the time-lapse digital still cameras was provided by Woods Hole Oceanographic Institution, and one was built by high school students from Hawaii as part of the Science Technology Engineering Mathematics education component of HUMMA. Because of the high probability of recovering toxic material (e.g., mustard gas), shipboard safety procedures were implemented and handled on site by the Army's Combat Capabilities Development Command, Chemical Biological Center personnel, as safety was a primary concern (UH and Environet 2016) (Edwards et al. 2016b).

A diversity of state-of-the-art technologies were used for the HUMMA study. Bathymetry was derived using a Kongsberg Simrad EM1002 multibeam, which operates at a frequency of 95kHz, mounted on the hull of the University of Hawaii (UH) research vessel. An IMI-120 phase-differentiated side-scan sonar towed at 50-75m altitude above the seafloor was also used. Two HOVs capable of achieving depths of 1000m were used in the project (Edwards et al. 2012; Carton et al. 2014; Edwards et al. 2016a).

HUMMA field programs were designed to collect water, sediment and biota samples to test for various chemicals of potential concern (COPCs) around DMM, including specific MC and associated MC degradation products related to chemical and conventional munitions. HUMMA COPCs fall into three general categories: CA and agent breakdown products from bomb fill materials; energetic materials from conventional munitions as well as explosive charges designed to rupture chemical munition casings (known as a bursters); and metals from munitions casings. The burster for M47A2 bombs had one of three possible fills: (1) 0.68 kg of TNT; (2) a 50/50 mix of black powder (a mixture of sulfur, charcoal, and potassium nitrate) and magnesium; or (3) TNT and tetryl pellets. In addition to the M47A2 bombs, thousands of conventional munitions were detected in the HUMMA study area. Based on knowledge about munitions high explosive fills from the WWII era, the energetic COPCs selected for HUMMA were TNT, RDX, tetryl and DNTs (Briggs et al. 2016; UH and Environet 2016).

In 2009 the HOVs collected sediment and water samples using a purpose-built clear PVC tube with a ball valve at one end (sediments) or both ends (water). The 2012 version of the samplers were clear, open-topped PVC tubes that were sealed with a T-bolt-handled PVC cap once enough sediment had been collected. Water samples collected during the 2009 HUMMA Sampling Survey had no detectable levels of MC; only five water samples were collected in 2012 to calibrate the deep ocean mass spectrometer and no water samples were collected in 2014.

The 2009 HUMMA program was designed to collect samples from four types of sites: control sites, which were >50 m from reflective targets in the backscatter data and from munitions observed by the HOVs' internal high-frequency sonars; dredge spoil sites, which provided an important comparison for other anthropogenic sources of COPCs; DMM sites in sandy/silty terrain; and DMM sites within the dredged material areas. As no chemical bombs (M47A2) were unambiguously identified before or during the 2009 HUMMA sampling survey, samples were collected around DMM that were likely conventional munitions. Nineteen sites were sampled in 2009 (Briggs et al. 2016). During the 2012 cruise, sediments were collected at multiple distances (0, 0.5, 1.0 and 2.0m) from each of the nine DMM sampled in linear transects from the nose, upper half of munitions casing, lower half of casing and tail to examine the spatial distribution of COPCs. Sediment samples penetrated 0-8cm into the sediment (Briggs et al. 2016). In addition, a Wildco Ekman Grab box corer (3540 cm³) was deployed once per study site to document benthic organisms contained within the sediments. Box corers were collected approximately 1.5 m from the DMM for benthic infauna evaluation.

4.5.1 Results

The integrity of DMM in the HUMMA study area spans a broad spectrum: the deterioration level of casings ranged from almost pristine to virtually disintegrated. The state of deterioration varied within similar munitions types located in the same general area, as well as between different types of munitions spread over a wide region. In general, munitions with thicker casings were better preserved. Most of the munitions casings visually studied were not obviously breached, although many DMM were imaged with skirts or columnar pedestals beneath them that may be the result of rusting, possibly in combination with leakage of internal MC. Generally, conventional munitions, because their thicker steel walls, are better preserved than the M47A2 bombs. The corrosion of sea-disposed munitions in the HUMMA study area remains poorly understood (Silva and Chock 2016).

Metals of potential concern in sediment throughout the HUMMA study area were generally below marine screening levels. Detectable concentrations of distilled sulfur mustard (HD) or its breakdown products, 1,4-dithiane, were found in sediments collected at each M47A2 bomb sea disposal site. Neither HD nor its breakdown products were detected at conventional munition

sea disposal sites. However, HD was also detected at two control sites. The only energetic compound detected during both the 2012 and 2014 HUMMA Sampling Surveys was 4-nitrotoluene (4-NT) (UH and Environet 2016).

Tissue samples of the shrimp *Heterocarpus ensifer* were analyzed for the presence of CA. However, CA was not detected. Of the energetics analyzed, TNT was the only COPC detected; 4-ADNT and TNB are manufacturing by-products of TNT or environmental transformation products were also detected. Each of the energetics was detected at low levels in shrimp during the 2012 and 2014 HUMMA sampling surveys. Nitrobenzene was also detected at low levels, with a possible source being transformation from TNB. Metal COPCs in shrimp tissue were detected at low levels and at a similar number of detections and range during both surveys. No visible deformities, eroded fins, lesions, or tumors were observed on the shrimp living in the vicinity of M47A2 bombs (Koide et al. 2016).

Given these results and under current and potential future uses of the HUMMA study area, health risks to likely receptors are within USEPA acceptable levels (UH and Environet 2016). Photographic data and benthic infauna analysis were used to study benthic organisms that lived on or near munitions. There was no statistically distinguishable difference between organism distributions in dense and sparse munitions fields. Conventional munitions were found to have the greatest number of benthic infauna individuals, with control sites generally having the least number of individuals. This is consistent with the benthic macro-fauna analysis, which shows that munitions provide habitat (UH and Environet 2016).

The overarching result from five HUMMA field programs conducted over a decade is that there is little evidence that leakage from munitions into the surrounding environment has a direct pathway to affect human health and the impact on the surrounding environment in Hawaii is detectable only at trace levels. This finding should be modulated based on the quantity of physical samples, which were collected around <1% of the potential 16,000 bombs. In 2014 when the Jason 2 ROV directly sampled the internal constituents of bombs, HD was detected in sediment at concentration close to the level of detection. Additionally, inconsistent with results from the 2009 and 2012 HUMMA sampling programs, during the ROV-based 2014 field program trace amounts of mustard agent and its breakdown products were detected at control sites. Both findings support a hypothesis that the impacts of sea-disposed munitions change over time.

5.0 STAKEHOLDER CHALLENGES AND PERSPECTIVES

5.1 Shaping Community Understanding of the Risks of Underwater Munitions: The Importance of Sound Science and Effective Communication

5.1.1 Introduction

Communities potentially impacted by underwater munitions often believe action is necessary because of explosive risk, chronic toxic risk from conventional explosives or small arms munitions, or an acute risk from a chemical agent. Requests for cleanup are tied to the confirmation of a potential pathway that depends on where items are located, their type, and the potential for natural or human-caused movement of items that would affect exposure (Siegel 2008). The community's willingness to accept assurances that risk levels are low, and cleanup is not warranted is a function of whether they trust the people offering the assurances (Siegel 2008). Community perspective is based on perception of exposure risk, which often differs from the perspectives of resource agencies focused on resource restoration.

An example of effective communications with the community comes from the Convention for the Protection of the Marine Environment of the North-East Atlantic known as the OSPAR Convention". Following WWI and II, large quantities of munitions were dumped in the OSPAR maritime area, including conventional munitions, phosphorus incendiary devices, and chemical munitions containing chemical agents such as sulfur mustard (Nixon 2009). The OSPAR Agreement (between numerous European countries) includes a framework for developing national guidelines for commercial fishermen on how to deal with encounters with conventional and chemical munitions, including providing information on areas at-risk, giving a general description of munitions and chemical agents and their effects and first-aid treatment, and what to do in the event of an encounter. In 2005, three commercial fishermen were killed in the southern part of the North Sea when a WWII bomb that was caught in their nets exploded on board their vessel (Nixon 2009). Commercial fishermen in the North Sea are considered most at-risk and the guidelines were updated after the 2005 incident (Nixon 2009). Commercial fishermen are supplied with a subsurface marker buoy for marking where munitions are encountered when trawling. This effort has been successful to date and has resulted in documentation of the locations of munitions, based on information from OSPAR (Nixon 2009).

5.1.2 States and Territories of the USA

States and territories rely on the federal government to perform investigations of underwater munitions' sites and undertake response actions. States are limited by a lack of personnel with

the expertise to evaluate potential hazards or provide adequate oversight of investigations. States are also limited by a lack of funding to independently investigate underwater munitions.

States and territories made the following recommendations for the Department of Defense (DoD) related to addressing underwater munitions and MC (State MRF 2013):

- DoD should work with Congress to develop a policy allowing for additional funding and more effective use of currently available funding;
- Funds should go toward research and development to better understand the potential risk posed by underwater munitions and MC;
- A national policy must be developed in order to ensure sites of suspected contamination are investigated in a timely manner;
- The DoD policy indicating that munitions at depths deeper than 120 ft should be reconsidered, particularly in areas where commercial and recreational fishermen may use deep water areas;
- DoD's Maritime Industry Safety Guide that educates commercial fishers about hazards from underwater munitions sites should be revised to recommend that recovered items be jettisoned but the location where they are jettisoned be recorded. The guidance should also be revised to include first-aid information;
- Education efforts should be expanded particularly for beach goers and fishermen; and
- Technology development for detection, characterization, and response is too far behind and should be further developed by DoD.

States and territories support the recommendations in (SERDP 2010) to:

- Conduct field data collections in several worst-case MR sites and use the data collected to support ecological risk assessment at sites;
- Develop a standardized approach to field data collection at underwater sites and a database to track sites and investigations; and
- Increase communication between DoD and other agencies engaged in underwater munitions work.

5.1.3 Non-Governmental Organizations and Business, Case Study: Offshore Wind Farms, Germany

There are thought to be millions of tons of munitions in German seas with many in coastal waters. For decades, these munitions posed little threat but there is now a growing wind farming industry and a push to expand offshore wind farms. Buried munitions are slowing the construction and expansion of these projects and the amount of munitions is proving far greater than expected, making it complicated to lay a submarine cable let alone install foundations for turbines. A recent

survey to look for discarded munitions along a 45-kilometer (km) route for cable operation to a wind park over 2,000 items and at least 350 of 600 targets were unexploded ordnance (<https://www.dw.com/en/wwii-bombs-explode-at-north-sea-wind-farm/a-16360735>).

In many cases, because of the type of fuse the items have, there is no safe way to transport them and they are BIP. Controlled detonation, even at the water surface, has impacts on marine mammals, which are common in the North Sea area where work is being conducted (including porpoises, gray seals and common seals). Detonations during the rearing phase of common seals in June/July or gray seals in December/January may cause mothers to flee the noise, abandoning their pups. Detonations can also rupture the lungs and eardrums of seals within a radius up to 4 km, and there can be impacts to an animal's hearing up to 10 km from a detonation due to the size of the munitions in the area (Detloff et al. 2012). A coalition of German environmental organizations are pushing for legal guidelines for dealing with controlled explosions (Long 2011). Ordnance disposal specialists, including those working for wind farm companies as consultants, agree that this would be helpful to ensure the protection of areas used by marine mammals and the animals themselves while also enabling projects to move forward more quickly. Environmental organizations and other non-governmental organizations are also calling for changes in methodology to move toward technologies using underwater robotics, water abrasive suspension cutting, or mobile detonation chambers rather than controlled detonations to further reduce the risks to marine life (Detloff et al. 2012; Long 2011).

5.1.4 Case Study: Vieques, Puerto Rico

On February 11, 2005, all portions of the former training area at Vieques, PR (Figure 5-1) were placed on the National Priority List, which required all subsequent environmental restoration activities for Navy Installation Restoration sites on Vieques be conducted under CERCLA unless and until removed from CERCLA authority. The Navy, Department of Interior (DOI), USEPA, and Puerto Rico Environmental Quality Board (now part of the Puerto Rico Department of Natural and Environmental Resources) executed a Federal Facility Agreement on September 7, 2007 that established the procedural framework and schedule for implementing the CERCLA response actions for Vieques. Since response activities began, members of the community have been vocal in their belief that cleanup efforts, as well as past training activities, are responsible for health problems and declines in fishery catch. The Navy and others, including NOAA, have conducted several studies that do not support these beliefs, indicating that communications efforts have not been successful and that the community does not trust the information they have received from the Navy and others who have led the studies (Table 5-1).

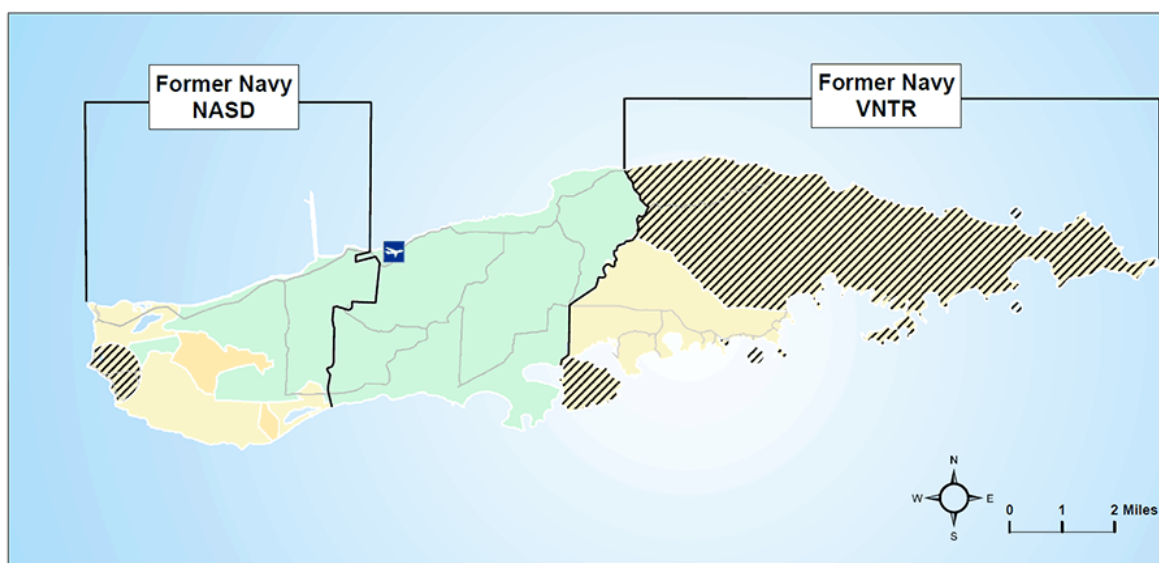


Figure 5-1. Map showing former eastern and western components of the former Atlantic Fleet Weapons Training Area.

Table 5-1. Public perception of impacts from cleanup, including terrestrial detonations, and existence of munitions in underwater areas at Vieques compared to scientific findings

Public Perception	Scientific Findings
Detonations lead to air pollution with serious health effects	Air sampling and modeling over 8 years during 177 detonations and 19 accidental brush fires detected no explosive chemicals, concentrations of metals at least 99% below health-based standards, and no violations of USEPA's National Ambient Air Quality Standards (from fact sheet summarizing results of air quality monitoring reports)
Fish species are highly contaminated, which is why catch has declined significantly after waters were opened to public	In 4 of 78 sites tested around Vieques, NOAA found Dichlorodiphenyltrichloroethane (DDT) at a level above accepted guidelines. At one site, chromium was detected at a level above accepted guidelines. No explosive compounds were detected and nutrients, fish populations, and coral reef ecosystem conditions were comparable to other areas of Puerto Rico (Whitall et al. 2016)
	Sampling of queen conch tissue for metals, DDT, and energetic compounds found no munitions compounds or DDT. Degradation compounds of DDT were found in one queen conch but there was no clear spatial pattern for conch data to indicate hot spots. Concentrations of metals were within range of values for other Caribbean sites (Whitall et al. 2016)

Table 5-1 (continued). Public perception of impacts from cleanup, including terrestrial detonations, and existence of munitions in underwater areas at Vieques compared to scientific findings

Public Perception	Scientific Findings
Land crabs on Vieques are contaminated due to military activities	PCBs and pesticides were detected in only a few samples. Levels of PCBs, organochlorine pesticides, and trace elements found in land crab samples were lower than levels reported to cause harmful health effects. No explosive compounds were detected in any samples. No association was found between sampling location and contaminant levels (ATSDR 2006)

Other studies conducted in nearshore marine areas of Vieques also found the impacts of the presence of munitions items and possibly MC to be minimal. Díaz et al. (2017) compared concentrations of lead, cadmium, and copper content in manatee grass collected from nearshore areas within the former Vieques training area with the same seagrass collected from nearshore areas within the Guánica Biosphere and Natural Reserve. The results indicated that, while bioaccumulated concentrations of metals in seagrass were consistently higher in samples from Vieques, the differences were not statistically significant between sites. However, there was an overall decrease in lead concentrations in seagrass samples from Vieques beginning in 2003 when military activities ceased.

Porter et al. (2011) found that concentrations of MC in sessile organisms such as feather duster worms and corals exceeded USEPA's Risk Based Concentrations for commercially edible seafood, but no concentrations were exceeded for mobile species like fish and lobster. In addition, the concentrations of TNT and chromium in sediment declined rapidly with distance from a munitions item and were undetectable 10 cm from a munitions item. While there is likely a health consequence for particular coral colonies and other sessile benthic organisms in the immediate area of a munitions item, the conclusion that substances are now widespread in the marine food web reached by Porter et al. (2011) is not supported by their analysis.

5.1.5 Conclusions and Recommendations

A community education program was created for Vieques, and the Navy and USEPA have project websites but there has been no usage tracking, testing of user's perceptions of the utility of the sites, or links to local websites that might be more visited by the local community. The results of scientific studies are posted to these websites and circulated to the community but there are no effectiveness metrics to determine whether the information is read and understood. Additionally, as discussed previously, there appears to be a lack of trust within the community

that leads to an unwillingness to believe information regarding human health risk and environmental impacts from munitions items.

As part of communication efforts, the Navy and USEPA should develop strong relationships with the local media and approach them first with topics that are likely to be of high interest to the community. An effort should also be made to use local scientists as the messengers when possible, or others who are likely to be better received by the community. A conceptual model for risk assessment should be developed and local researchers should be used to the extent possible to perform and assist in field sampling and laboratory analyses. The education program should be refined to target specific user groups and give them tools to assist with scientific studies and reporting of locations of munitions. Educational tools should also be developed based on education level/literacy of target audience, as well as culture, and social media should be used as a tool to keep the public informed. As cleanup efforts progress and begin to focus more on the marine environment, it will be important to improve communication with the community and to have their support not only for cleanup efforts, but for decisions to leave items in place in areas where their removal might result in greater harm to marine resources such as corals.

5.2 Role of Natural Resource Trustees in Munitions Response

The United States of America has enacted a suite of laws to address the degradation of the natural environment. The CERCLA and the Oil Pollution Act (OPA) authorize the United States, States, and Native American Tribes to act on behalf of the public as Natural Resource Trustees, often referred to as “trustees”, for natural resources under their respective trusteeship.

CERCLA requires the President to designate in the National Contingency Plan (NCP) Federal officials who are to act on behalf of the public as trustees for natural resources under Federal trusteeship. The NCP designates the Secretaries of the following Cabinet Departments to act as trustees for the natural resources, subject to their respective management or control: The Department of Commerce, DOI, Department of Agriculture, DoD, and the Department of Energy.

The trustees work to evaluate the risk to natural resources from the release of oil or other hazardous substances, including munitions constituents, as part of the site investigation or remediation. Trustees use Natural Resource Damage Assessments to assess any injuries to natural resources held in the public trust and ensure any resources injured are restored, replaced or that the equivalent are acquired.

Trustees quantify environmental injuries and work with the response authorities to make sure those resources are restored. Natural resource trustees work in partnership with regulatory agencies (e.g., USEPA) to review Remedial Investigation work plans, Remedial Investigation data,

and proposed cleanup plans throughout the remedial process. Data generated during Remedial Investigations are used to evaluate injuries to natural resources. Trustees may also conduct their own natural resource injury studies. Trustees also provide recommendations on how natural resource injuries can be avoided or minimized during the site investigation or cleanup process.

As the primary federal trustee for coastal resources, the National Oceanic and Atmospheric Administration (NOAA), acting on behalf of the Department of Commerce, has the responsibility for ensuring the restoration of coastal resources injured by oil and hazardous substances, as well as national marine sanctuary resources injured by physical impacts.

NOAA's Office of Response and Restoration provides scientific support to the USEPA, the Puerto Rico Environmental Quality Board (PREQB), the U.S. Fish and Wildlife Service (USFWS) and the U.S. Navy on the ongoing investigation and cleanup of Vieques Island, PR. In addition, in fiscal years 2005 through 2007, NOAA received appropriations from Congress to assist the Departments of Defense and Interior, and USEPA and PREQB, in facilitating the cleanup, protection and restoration of the coastal and marine resources of Vieques. In collaboration with federal and commonwealth partners and the Vieques community, NOAA implemented the following projects:

5.2.1 Ecological Characterization of the Marine Resources of Vieques

NOAA conducted a two-phase effort to characterize the marine resources surrounding Vieques Island. Part I of the study contains a summary of existing data on the physical environment, habitat types and associated fish and invertebrate communities (Bauer et al. 2008). Part II of the study builds on the Phase I work presenting new data on benthic features, biological communities, nutrients and contaminants (Bauer and Kendall, 2010). The study provides baseline data to determine the health of the coral reef ecosystems in Vieques and will help in the development of a strategy for long-term monitoring of Vieques' coral reef ecosystems supporting the cleanup and protection of the resources.

5.2.2 Underwater Unexploded Ordnance Demonstration Project

NOAA conducted a hydrographic survey to demonstrate the effectiveness of side-scan and multibeam sonar, magnetometer, and video mosaic imaging in identifying ordnance and related debris in the waters around Vieques. This demonstration project helped the Navy evaluate technology capabilities and guides planning for future hydrographic surveys.

5.2.3 Coral Reef Restoration Demonstration Project

NOAA completed a demonstration project to evaluate the success of various techniques to restore coral reefs in Vieques, such as transplantation of coral fragments and coral larval

recruitment to artificial substrates. The data will be applied to the future cleanup and restoration of the coral reefs.

5.2.4 Land and Fiddler Crab Study

NOAA conducted an investigation to characterize chemical concentrations of hazardous substances in land and fiddler crabs on Vieques. The Agency for Toxic Substance and Disease Registry (ATSDR) concluded that eating land crabs on Vieques does not pose a human health risk (ATSDR, 2006). The results assisted USFWS in their determination of whether refuge areas could be opened to the harvesting of land crabs. The land and fiddler crab data are also being used as part of the cleanup investigation.

5.2.5 Other Activities

NOAA also assisted in sample collection taking place as part of the ongoing Remedial Investigation activities and continues to collaborate with the U.S. Navy on activities such as locating munitions underwater, determining risks associated with underwater munitions, and evaluating remedial actions.

NOAA also assisted the U.S. Army on the ongoing investigation and cleanup of Culebra, PR. NOAA has reviewed Remedial Investigation work plans for the various MR sites activities, provided technical support for coral surveys and underwater munitions surveys, and recommendations regarding cleanup activities

In addition to its munitions-related activities in Puerto Rico, NOAA provides support to the U.S. Army on sea-disposed munitions activities in Hawaii. These efforts focused on minimizing impacts to coral during the development and demonstration of the Remotely Operated Underwater Munitions Recovery System at Ordnance Reef, Oahu, HI. Because NOAA and the U.S. Army believed the demonstration to remotely remove underwater munitions, particularly the use of a ROV, would result in unavoidable impacts to coral, NOAA partnered with U.S. USACE to help it avoid or minimize such injuries and to assess any injuries that occurred during the project. NOAA mapped the locations of coral and munitions prior to munitions removal. NOAA then quantified the injuries to coral and is working with the Army to develop an appropriate coral mitigation strategy commensurate with the injuries that occurred.

NOAA Fisheries is also providing technical assistance to DoD to ensure compliance with the ESA for underwater and terrestrial cleanup activities around Vieques and Culebra. The ESA provides a means whereby the ecosystems upon which threatened and endangered species depend may be conserved and a program for the conservation of threatened and endangered species. All Federal agencies are required to consult with the USFWS and the National Marine Fisheries

Service (NMFS) to carry out programs for the conservation of threatened and endangered species (Section 7(a)(1)) and to insure that any action authorized, funded, or carried out by the agency is not likely to jeopardize the continued existence of any threatened or endangered species or result in the destruction or adverse modification of designated critical habitat for listed species (Section 7(a)(2)). In this role, the NMFS has provided technical assistance to DoD toward the development of standard operating procedures for surveys and cleanup efforts that are not likely to adversely affect ESA-listed species or designated critical habitat. NMFS is also engaging in programmatic ESA section 7(a)(2) consultations with DoD agencies for underwater cleanup activities around Vieques and Culebra to streamline ESA consultation processes.

5.3 Navy Munitions Response Site Challenges and Management

The Navy's underwater Munitions Response Program (MRP) has multiple challenges including the detection, location, and remediation of UXOs. Per policy, the program addresses shallow water areas where munitions releases are known or suspected to have occurred and where: 1) Navy actions are responsible for the release, and 2) munitions are covered by water no deeper than 120 feet. Munitions located in waters between high and low tides are managed as terrestrial. Sites are not a part of the Navy's MRP if they are:

- Part of, or associated with, a designated operational range
- A designated water disposal site
- A FUDS
- A result of combat operations
- A maritime wreck
- An artificial reef

Currently, the vast majority of the Underwater Environmental Restoration Navy (ER,N) Munitions Response sites included in Military Munitions Response Program (MMRP) are in the Site Inspection (SI) phase. The Remedial Investigations (RI)/Feasibility Studies (FS) for these sites are currently planned to start in 2023.

Funding and site management may be either by the ER,N program or Base Realignment and Closure (BRAC) program. It estimated that Phase 4 (Remedial Action) costs are greater than \$1.3B for 57 sites or Areas of Concern (AOCs) in the Navy program. Site assessment and cleanup requires an explosive hazard assessment and assessments of human health and ecological risk, the explosive hazard must be assessed on a site-specific basis. There is no standard assessment procedure for assessing explosive hazard. For MC, existing risk assessment guidance are followed for both human health and ecological assessments.

The Navy's MRP underwater sites have highly diverse site settings and characteristics. For example, sites include ponds, rivers, lakes, intercoastal waterways, and oceanic locations. They are in shallow to deep water, and vary in terms of currents, wave action, tides, water clarity, turbulence, and other factors. Typical weather considerations are also variable. Bottom types include hard and soft with varying sediment characteristics. Examples of habitat and biota include sea grass beds, coral reefs, open bottom, wetlands, and marshes. Human use also varies greatly, with intensive current use near population centers to little current activity at remote locations. The types of munitions present vary according to the types of sites (e.g., ranges) and the historical military activities that occurred. (ranges, manufacturing, transportation, and handling).

Some examples of underwater MRP sites include the following:

- Jackson Park Housing Complex – Performed ammunition manufacturing, transportation, storage and demilitarization. Releases occurred along the piers and shoreline adjacent to housing complex;
- Former Mare Island Naval Shipyard – Performed ammunition loading and OB/OD operations. Releases occurred along piers and from kickouts from the OB/OD operations;
- Vieques National Wildlife Refuge – Performed ammunition storage and was a Live Impact Area (LIA) for munitions. Releases occurred from numerous offshore impacts in shallow near shore zone;
- San Diego Bay Primary Ship Channel – Releases occurred from munitions loss overboard, ship sinking, aircraft accidents, ammunition handling, and training operations; and
- Cat Island Bomb Target – A former bombing target in low lying marshy island with recreational fishing and boating nearby.

An example MR conceptual site model is provided below (Figure 5-2) from the San Diego Bay Site 100 SI (San Diego Site 100 SI). It includes multiple aspects associated with the site, including source, release mechanisms, exposure media, migration and transport, secondary exposure media (including surface water and sediments), exposure pathways, and potential receptors (including divers, beach users, ship crews, fish and bay floor sea life, boaters and swimmers).

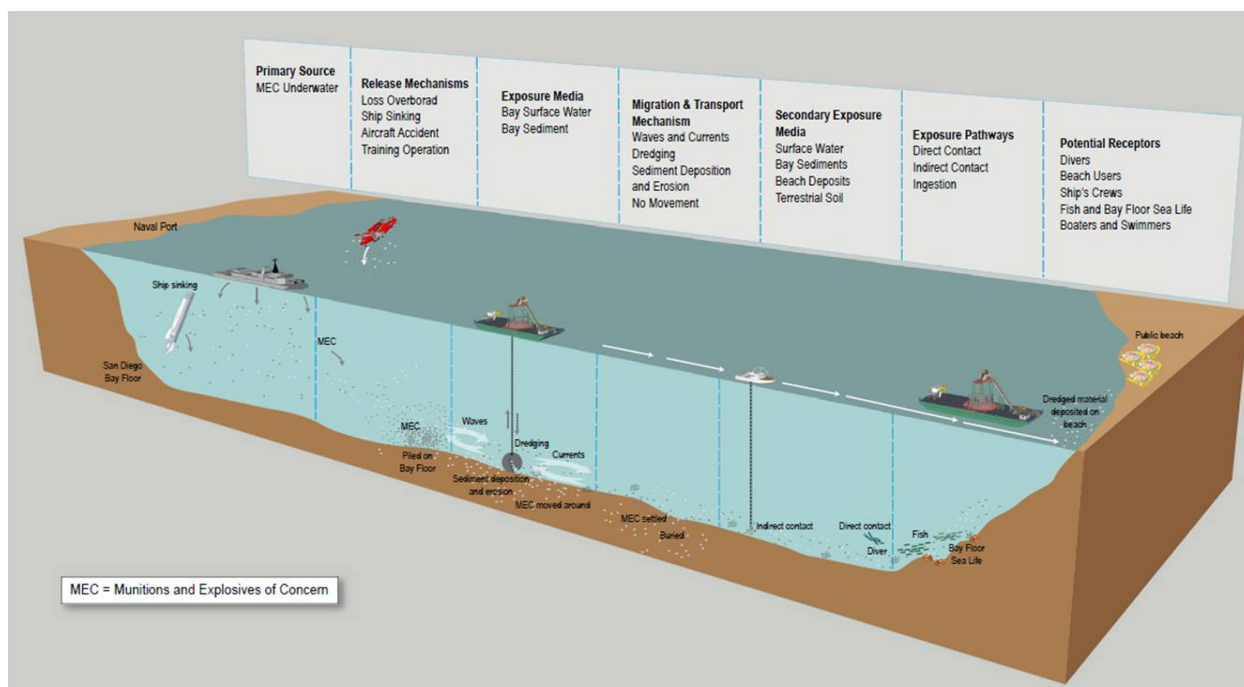


Figure 5-2. Conceptual site model for MRP sites.

One of the challenges encountered in the investigation of underwater MEC is the poor visual clarity to assess the site to determine locations of any MEC. This can require the use of metal detectors at the site. When magnetometers and electromagnetic induction devices are used, detection capability is constrained and hampered by the degree of metallic clutter in the area. A large amount of metallic debris is typically present along the piers, posing challenges to the location of munitions within the debris. In addition, dive operations are much slower than terrestrial operations and safety measures pose additional challenges to address the MEC. There are diving restrictions in certain locations and times due to high currents. Another challenge is the diver determination of the status of the fuzing for items that are heavily encrusted, so one resorts to information about the site history. If the site was a range, then the item is treated as UXO. If it was a DMM site, the items are treated as those typically disposed. Open detonations are a common method of disposal for UXOs. Significant impacts, such as destruction of corals, may occur at detonation events. Other underwater considerations including making sure the marine animals are removed or otherwise safe prior to detonation. Another challenge is the state of corrosion the item is in, which was discussed in Section 3.1.2. The corrosion rate is site and item-specific, being modified by factors such as burial or lying proud on the bottom. Estimated rates of corrosion at one site noted that items may not breach for up to 500 years. On water ranges, such things as dud rates will be site-specific as well.

Currently, numerous SERDP projects (<https://www.serdp-estcp.org/Program-Areas/Munitions-Response/Munitions-Underwater>) are investigating the potential for underwater MEC to move

and migrate in underwater environments, such as in the surf zone, in bays and deeper offshore. It appears that since most MEC are dense, that they tend to bury, but this is still an area of active research. The depth of burial can impact detection capabilities, particularly for metal detectors.

An additional concern regarding biological assessment is that some fish species have large ranges (i.e., limited site fidelity) and may be exposed over large areas. Collection and chemical analysis of fish from the site does not necessarily reflect site exposure.

There is a need for a conceptual site model that makes sense with respect to fish tissue concentrations based on the fact that many fish species are not necessarily in routine contact with water or sediments contaminated by MC. This is a substantial challenge for Navy program managers, who are faced with the complexities associated with how and when to sample, how to design a sampling program with items that are in various phases of corrosion and exposure to receptors in underwater environments. Along with these complexities, the project manager has to address the significant hazard/risk to UXO divers attempting to remediate the MEC.

6.0 GROUP DISCUSSION AND RECOMMENDATIONS

The overall goal of this workshop was to seek resolution on key questions and narrow/refine outstanding issues related to environmental risks associated with UWMM. This involved bringing together scientific experts and stakeholders (e.g., site managers, regulators) to present and discuss the existing scientific evidence regarding environmental risks posed by UWMM, uncertainties associated with these risks, and remaining challenges to validate risk conclusions at UWMM sites. Group discussion during the meeting resulted in several conclusions on some data gaps, along with general recommendations on where future research may be warranted.

1) Corrosion of UWMM in aquatic environments

Corrosion is one of the most relevant elements determining the state of UWMM, which in turn is a determining factor on the incidence of release of MC into the surrounding environment and the release rate, if occurring (see Section 2.1.2 of this report). The following considerations on corrosion of UWMM were made by workshop participants during discussion periods:

- Accounts exist of similar munitions sitting in close proximity to each other at UWMM sites with one appearing nearly pristine and the other appearing corroded and degraded. The causes of these differences are uncertain, given that munitions may have been produced over 100 years ago. Steel production techniques may be a contributing factor such as inadequate mixing, etc. Differences in biofouling, sediment type, and various other environmental variables that are site-specific may also contribute to differences.
- *In situ* quantitative corrosion rate studies have been conducted in the Baltic Sea (e.g., Jurczak and Fabisiak 2017). It does not appear there are any quantitative *in situ* underwater corrosion rate studies in the U.S.

Recommendation:

- *In situ* quantitative corrosion rate studies at UWMM in the USA are warranted.

2) Prediction of MC concentrations in the water column at UWMM sites

The Shell Model, developed under [SERDP project ER-1453](#), defines the estimation of the mass of MC that is released from the breached shell into the water column and sediment (Wang et al. 2011, 2013). The Shell Model provides a way to quantify the fundamental processes that govern the MC release from a single shell, which can then be applied to an ensemble of shell types and conditions at a site. The Shell Model has also recently been successfully validated empirically (Lotufo et al. 2019). A methodology was recently developed to extend the Shell Model to address a large number or distribution of breached shells at a site (Lotufo et al. 2017). Workshop participants expressed that substantial uncertainty seems to plague approaches to predict the range of concentrations of MC in the water column at UWMM.

Recommendation:

Research to address uncertainty concerning the rate of release from multiple munitions at UWMM sites and model predictions of water column concentrations. Future research should include coupling the Shell Model with fate and transport models for UWMM sites for comparisons of predicted and empirical site data.

3) Sampling methodology

A wide range of methodologies have been employed to obtain water, sediment and biota samples at UWMM sites around the world (Section 2.3 of this report). The only known guidance document for sampling MC at the UWMM sites is provided in Rosen et al. (2017b) for passive samplers deployed in the water column. The following considerations on sampling at UWMM sites were made by workshop participants during discussion periods:

- The concentrations of MC in sediment were overall low and below preliminary benchmarks for effects to the benthic biota, with high concentrations reported only for a small fraction of the samples (Section 3.1.2 in this report). The reported high degree of spatial heterogeneity in contamination is similar to that reported for terrestrial sites (Pichtel 2012).
- The use of passive samplers has been successfully demonstrated at a UWMM site (Section 2.3.2 of this report). In addition, USEPA funded research on the development of passive samplers for MC is currently underway (Rakowska et al. 2019).
- Passive samplers demonstrated for use at UWMM site are not currently appropriate for picric acid and related compounds.
- To characterize contamination in sediment, the use of passive samplers is recommended for highly hydrophobic organic compounds. However, for MC, concentrations in pore water can also be measured directly (e.g., Rosen et al. 2017a) as organic carbon-water partition coefficients are low and thus mass flux issues are not problematic as for hydrophobic organic.

Recommendations:

- A modification of the incremental sampling method (ISM; also referred as multi-increment sampling) technique (USEPA 2006) used at terrestrial sites (e.g., Hewitt et al. 2009; Clausen et al. 2018) to characterize MC contamination at UWMM sites is warranted.
- The development of specific guidance for sampling water and sediment at UWMM sites should be considered.
- Further development of passive sampling techniques to include sampling of picric acid and related compounds should be considered.

4) Water column MC contamination at UWMM sites

Considerable evidence indicates that relatively high concentrations of MC may occur a short distance (e.g. up to 10 cm) away from munitions with concentrations rapidly declining away

from the munitions to low detected levels or to non-detects (e.g., single- or double-digit parts per trillion) (e.g. Ampleman et al. 2004, Ochsenbein et al., 2008, Porter et al. 2001, Rosen et al. 2017a, Rosen et al. 2018, see section 3.1). For UWMM sites for which water column concentrations were reported, concentrations of MC in the water column were below levels indicative of potential risk to biota exposed to the water column (Section 2.4.1 of this report). Therefore, existing information should be used when planning sampling and analysis of the water column to adequately characterize exposure at sites with similar characteristics as those already investigated. The following considerations on water column MC contamination were made by workshop participants during discussion periods:

- The assumption of low contamination at UWMM is more applicable for open water sites or those with flowing water. Concentrations of MC in the entire water column are more likely to exceed risk criteria in smaller bodies of water, such as near coastal lagoons and lakes where leaking UWMM are present.
- The results from sampling studies conducted in Vieques, PR (Rosen et al. 2017a) and elsewhere (e.g., Kolberger Heide site in Germany, Beck et al. 2019) could be extrapolated for other water ranges with similar operations. It would thus seem reasonable to assume the MC is localized around individual pinpoints of contamination (i.e., in very close proximity to munitions or formulation fragments). The major difference between Vieques and Kolberger Heide and other sites is the water clarity. It is relatively easy to select sampling locations next to unburied UWMM at Vieques. At sites with poor visibility, the ability to find and detect UWMM is questionable, with buried items unlikely to result in detectable concentrations in the water column. Therefore, a sampling scheme that excludes sampling near UWMM is most likely going to result in non-detects or detection at ultra-low parts per trillion concentrations.
- All sites are unique, and every site under investigation should be sampled to a degree that allows appropriate ecological risk assessment and satisfies the stakeholders and scientific objectives. Existing studies and their findings, used cumulatively and in an integrated fashion, should certainly be used as guidance for developing a sampling strategy and analysis at a specific site.

Recommendations:

- Development of a synthesis paper on MC in water that lays out the consensus on the contaminant risks and long-term risk management focusing on ecological receptors. This could lay the foundation for the reasonable path for newly investigated sites.
- Considering the size of sites and uncertainty with being able to identify and sample MC from the vicinity of UWMM, guidance needs to be provided towards developing a robust sampling plan. Guidance for both short-term site characterization and for long-term monitoring plans are needed.
- The development of guidance for some version of MNR for UWMM sites should be considered.

4) Accumulation of MC in biota at UWMM sites

Despite the low propensity of MC to bioaccumulate in fish and invertebrates via exposure to water and sediment (Lotufo et al. 2009a; Lotufo et al. 2013; Lotufo et al. 2016, Ballentine et al. 2015, 2016), MC has been found in biota inhabiting UWMM sites (Section 3.1.3 of this report). The use of biota contamination data is complicated by the paucity of tissue-based toxicity metrics used to assess the proper selection of toxicity reference values for assessing risk of MC. For the above reasons, an attempt to evaluate risk at UWMM sites using available biota data has not been made. Therefore, ecological risk assessment of MC at UWMM should be conducted based on site-specific information on the distribution of MC in the water column and sediment and comparison with benchmarks values and protective concentrations (Section 3.2 of this report). The following considerations on bioaccumulation of MC in biota at UWMM sites were made by workshop participants during discussion periods:

- Biota MC bioaccumulation data are needed for conducting human health risk assessment at UWMM sites.
- For some UWMM sites, concentrations in the water or sediment were mostly below detection, but concentrations in biota tissues were higher than would be expected considering the low propensity of MC to bioaccumulate in fish and invertebrates. Therefore, uncertainty exists regarding the accuracy of those measurements (i.e., possibility of false positives potentially attributable to issues with sampling methods).
- More standardization of tissue analysis methods to optimize detection limits are needed.

Recommendations:

- A field study involving paired tissue sampling and co-located passive diffusion samplers to improve our understanding of bioaccumulation of MC under *in situ* conditions should be considered.
- Since the workshop, recently developed methods to optimize detection of MC in complex matrices such as sediment and biota have been published (Craig et al. 2019; Crouch et al. 2019; Gledhill et al. 2019) (see Section 2.4. in this report). The use of these methods is recommended for the analysis of MC in biota collected from UWMM sites in future studies as they have been shown to produce more accurate results compared to methods used in earlier investigations.

5) Toxicity of MC to aquatic biota

Broad and comprehensive overviews of the toxicity of MC to aquatic biota are available (Lotufo et al. 2013, 2017). The following considerations regarding aquatic toxicity of MC were made by workshop participants during discussion periods:

- Insufficient toxicity data are available for nitrophenols (e.g., picric acid, dinitrophenol and their transformation products) while many sites have a fair amount of Explosive D (ammonium picrate), for which a large number of degradation products and intermediaries exist.

- Only provisional water quality criteria are available for MC and protective concentrations based on species sensitivity distributions. However, available toxicity data have been compiled with which to develop such criteria (e.g., USEPA criteria).
- Insufficient toxicity data are available regarding interactive effects among multiple MC and chronic toxicity.
- No information exists on the effects of chronic exposure to MC in corals and sublethal effects that in turn adversely affects populations.
- No information exists on MC endocrine disrupting, teratogenic or mutagenic effects on corals.
- No information exists on the effect of MC on mesophotic corals.
- The Munitions Items Disposition Action System (MIDAS) should be consulted regarding compounds used in various munitions.

Recommendations:

- Prioritize the data gaps identified by workshop participants at the meeting based on relevance for use in the risk assessment at U.S. UWMM sites.
- Generate definitive species sensitivity distributions to estimate protective concentrations (PC) (e.g., the PC₉₅ is the protective concentration for 95% species) for use in ecological risk assessment of UWMM sites.
- Engage USEPA towards development of ambient water quality criteria for key MC for both freshwater and marine environments

6) Assessment of ecological risk at UWMM sites

The available information indicates that negligible risk is predicted for aquatic biota exposed to MC at UWMM sites, with the exception of sessile organisms living directly on, or in very close proximity to, the breach on a munition or munition pieces (See Section 3.2.1). Similarly, risk has been predicted to be negligible for benthic invertebrates exposed to MC in sediment at UWMM sites, except for only a small subset of the sites (See Section 3.2.2). The following considerations on ecological risk assessment of MC at UWMM sites were made by workshop participants during discussion periods:

- In the context of the ESA, concentrations of MC could produce adverse effects, including mortality or chronic effects such as impacts to reproductive fitness or growth. For ESA-listed species that are also impacted by other stressors, exposure to MC could lead to local population declines. Therefore, risk assessments should include evaluations of the presence of MC in areas where ESA-listed species are present, particularly benthic organisms such as corals, and should include individual organisms or colonies of listed species.
- Site-specific ecological risk assessment should be largely based on site characterization data (i.e., information derived from relevant samples taken from the site) rather than modeled data.

- The spatial scale of the exposure and effects should be explicitly considered in ecological risk assessment for UWWM sites.

Recommendation:

The design of future risk assessments related to MC should consider the above points which incorporate specific recommendations.

7) Addressing concerns of local communities using natural resources from UWWM sites

Communities potentially impacted by underwater munitions often believe action is necessary because of explosive and ecological risks. A community's willingness to accept assurances that risk levels are low, and cleanup is not warranted is a function of whether its members trust the individuals or organizations offering the assurances. Community perspective is based on perception of exposure risk, which often differs from the perspectives of resource agencies focused on resource restoration (see Section 4.1.5 of this report). The following considerations on concerns of local communities were made by workshop participants during discussion periods:

- The use of more independent experts (e.g., local university scientists) could provide learning sessions about MC to address the major points: trust and information. The approach requires shaping the message based on the local communities and their cultural differences.
- The public often has perceptions about risk drivers that are not based on reality. It is important to ensure that the science and engineering knowledge is effectively communicated so that a discussion of the community concerns can be productive.
- Long-term monitoring of these sites is needed to take the concerns of the public into account and address them.
- Without proper communication, the public is likely to continue to have unwarranted concerns about MC that are based on misunderstandings of how munitions and MC actually behave underwater. Regulatory agencies, natural resources agencies, and the lead DoD agencies can move projects forward by emphasizing the results of current research on underwater MC.
- Proper risk communication will help stakeholders understand the actual risk posed by MC and properly understand the impact of other stressors to the local ecosystems such as overfishing of spawning areas and climate change.
- Site managers should effectively communicate to the public that limited resources could be more beneficially spent on identifying and removing explosive hazards rather than on additional site characterization, where applicable.

Recommendations:

A white paper with recommendations from risk communication experts in consultation with end users should be developed. The white paper would be expected to help focus the approach on how to effectively engage local communities and communicate complex scientific concepts.

8) Remedial actions and monitored “no action” at UWMM sites

Underwater actions related to UWMM to date were generally focused on the potential explosive hazard, not MC contamination of the underwater environment. A variety of remedial alternatives, including both *in situ* and *ex situ* approaches have been utilized or are under development (see Section 2.8 of this report). The following considerations on remedial actions and monitored “no action” at UWMM sites were made by workshop participants during discussion periods:

- Water jet cutting is a technology successfully used on land-based munitions. Technology towards underwater cut and capture systems to remove MC *in situ* is currently in development and demonstration under [ESTCP MR18-5116](#) (Schmidt et al. 2020) as a potentially much less destructive approach when compared with BIP or traditional removal methods that involve significant blast risks.
- Remedial actions at UWMM sites where UWMM are heavily relied upon as substrate for benthos, especially corals, will be highly site-specific, and could be dependent on the nature of the items and the potential explosive hazard. Different scenarios could dictate the remedy: 1) if munitions were discarded unfuzed, and are not attached to coral, they could be brought to the surface and disposed of on land; 2) if munitions are UXO and are rolling around or likely to come ashore, they could be attached to a floatation device, brought to the surface and detonated on a barge that would mitigate the blast wave in the water; and 3) if munitions are stationary and have been incorporated into reefs, they could potentially undergo a water jet cut and capture MC removal if that technology has been proven to be adequate for the site. Removal by BIP can destroy essential habitat and is generally not recommended.
- No remedial action (i.e., leave in place) could be the best choice when considering ecological risks alone as the risk to the local biota need to be considered relative to the damage caused by the remedial action. UWMM heavily used as substrate for benthos, especially corals could be left alone and possibly monitored using conventional water and sediment sampling or passive samplers.

Recommendations:

The development for “no action” focused guidance for UWMM sites should be considered. The guidance could be modeled after that developed under ESTCP Project ER-0622 (Magar et al. 2009). Variants of MNR such as Enhanced Monitored Natural Recovery (EMNR) should also be considered, which could combine a more cost-effective remedy (e.g. removal or treatment of select items to reduce unacceptable ecological risks by MC, followed by long-term monitoring to ensure acceptable remediation has been adequately achieved.

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8.0 APPENDIX

8.1 Workshop Agenda

WEDNESDAY, MAY 23, 2018		
0800	Arrival/Check in/Coffee	
	Opening and UWMM Overview	
0830	Welcome, introductions, and overview of SERDP/ESTCP including funded research on UWMM	Dr. Andrea Lesson, Deputy Director and Environmental Restoration Program Manager, SERDP/ESTCP
0850	Risk-informed decision making	Dr. Todd Bridges, U.S. Army Engineer Research and Development Center
0910	UWMM: A historic and geographical perspective	Mr. Geoff Carton, CALIBRE
0935	Shaping Community Understanding of the Risks of Underwater Munitions: The Importance of Sound Science and Effective Communication	Dr. Lisamarie Carrubba, NOAA Fisheries Office of Protected Resources
0955	Coffee Break	
	Session 1: State of the Science	
1015	Overview of munitions constituents (MC), munitions fillers and pathways of MC introduction to aquatic environments	Dr. Robert George, SPAWAR Systems Center Pacific
1040	Tracing the fate of the energetics released in temperate marine ecosystems	Dr. Craig Tobias, University of Connecticut
1105	Overview of MC in water, sediment and biota, toxicity to aquatic biota and derivation of protection levels	Dr. Guilherme Lotufo, U.S. Army Engineer Research and Development Center
1135	Toxicity of MC on corals	Dr. Cheryl Woodley, NOAA
1155	Bioaccumulation and toxicity potential of MCs	Dr. Mark Johnson, U.S. Army Public Health Center
1220	Lunch	
1315	Sampling and analytical strategies for water, sediment and biota	Mr. Gunther Rosen, SPAWAR Systems Center Pacific/Dr. Jason Belden, Oklahoma State University
1350	Group Discussion 1	-
1500	Break	
	Session 2: Stakeholder Challenges and Perspectives	
1515	Navy munitions response site challenges and management perspective	Mr. Bryan Harre, NAVFAC Engineering and Expeditionary Warfare Center
1545	Formerly Used Defense Sites (FUDS) Military Munitions Response Program (MMRP) Site Challenges and Management Perspective	Mrs. Deborah Walker, USACE Environmental and Munitions Center of Expertise

1615	Group Discussion 2	-
1700	Adjourn	
THURSDAY, MAY 24, 2018		
0800	Arrival/Check in/Coffee	
	Session 2: Stakeholder Challenges and Perspectives (cont.)	
0830	Role of natural resource trustees in munitions response	Ms. Diane Evers, NOAA Office of Response and Restoration/Dr. Lisamarie Carrubba, NOAA Fisheries Office of Protected Resources
0850	The science and suspicions of MC contamination at ranges	Mr. Stacin Martin, NAVFAC Atlantic
0920	Investigating and monitoring sea-disposed munitions at shallow- and deep water sites near Oahu, Hawaii	Dr. Margo Edwards, University of Hawaii
0950	Coffee Break	
1010	Remedial action decision making for the Navy Jackson Park underwater munitions site	Mr. Harry Craig, USEPA Region 10
1035	Removal challenges/blast risk	Mr. Steve Hurff, NAVFAC Headquarters
1100	Group Discussion 3	-
1200	Lunch	
1300	Group Discussion 4	-
1500	Break	
1520	Summary, Proceedings Schedule, Concluding Remarks	-
1600	Adjourn	

8.2 Attendee List

Last Name	First Name	Affiliation	Location
Belden	Jason	Oklahoma State University	Stillwater, OK
Bridges	Todd	U.S. Army Engineer Research and Development Center	Vicksburg, MS
Burgess	Robert	USEPA National Health and Environmental Effects Research Laboratory	Narragansett, RI
Carpenter	Angela	USEPA Superfund and Emergency Management Division	New York, NY
Carrubba	Lisamarie	NOAA Fisheries, Office of Protected Resources	Boqueron, PR
Carton	Geoff	CALIBRE Systems, Inc.	Baltimore, MD
Cloe	Kevin	Naval Facilities Atlantic	Norfolk, VA
Craig	Harry	USEPA Region 10	Seattle, WA
Cubero	Wilberto	USACE Jacksonville District	Jacksonville, FL
Cutt	Diana	USEPA Office of Research and Development	New York, NY
D'Auben	Michael	USACE Support Center	Jacksonville, FL
Doer	Brett	Jacobs Engineering Group Inc.	Doer
Dontsova	Katerina	University of Arizona	Tucson, AZ
Edwards	Margo	University of Hawaii Applied Research Laboratory	Honolulu, HI
Evers	Diane	NOAA Office of Response & Restoration	New York, NY
Fernandez	Loretta	Northeastern University	Boston, MA
Flaherty	Nancy	USACE HQ	Huntsville, AL
Frey	Bryan	Army Management–Installation Services Environmental	Washington, DC
George	Robert	Naval Information Warfare Center Pacific	San Diego, CA
Grossman	Scott	USEPA Environmental Response Team	Grossman
Harre	Bryan	Naval Facilities Engineering and Expeditionary Warfare Center	Pt. Hueneme, CA
Hood	Daniel	NAFAC Atlantic	Norfolk, VA
Hurff	Steve	NAVFAC Headquarters	Pt. Hueneme, CA
Johnson	Mark	U.S. Army Public Health Center	Edgewood, MD
King	J.C.	Office of the Deputy Assistant Secretary of the Army for Environment, Safety and Occupational Health	Washington, DC
Leeson	Andrea	SERDP & ESTCP	Washington, DC
Longberg	Kelly	USACE Support Center	Jacksonville, FL
Lotufo	Guilherme	U.S. Army Engineer Research and Development Center	Vicksburg, MS
Maddox	Doug	USEPA Headquarters	Washington, DC

Last Name	First Name	Affiliation	Location
Martin	Stacin	NAVFAC Atlantic	Norfolk, VA
Mollin	Jessica	USEPA Region 2	New York, NY
Montgomery	Michael	U.S. Naval Research Laboratory	Washington, DC
Nazario	Don	EcoAnalysts, Inc.	Lancaster, PA
Nelson	Herb	SERDP & ESTCP	Washington, DC
Nenninger	Philip A.	NAVFAC Northwest	Silverdale, WA
Opdyke	Cliff	USACE Baltimore District	Baltimore, MD
Pensak	Mindy	USEPA Region 2	Edison, NJ?
Pocze	Doug	USEPA Region 2	New York, NY
Rakowska	Magdalena	formerly with USEPA NHEERL	Narragansett, RI
Rodgers	Teresa	USACE Sacramento District	Sacramento, CA
Rodriguez	Danny	USEPA Vieques Field Office	Vieques, PR
Rosen	Gunther	Naval Information Warfare Center Pacific	San Diego, CA
Shipley	Emma	University of Connecticut	Groton, CT
Sivak	Michael	USEPA, Mega Projects Section	Queens County, NY
Strawhecker	Judith	USACE Omaha District	Omaha, NE
Taylor	Susan	U.S. Army Engineer Research and Development Center	Hanover, NH
Thompson	Tim	SEE, LLC	Seattle, WA
Tobias	Craig	University of Connecticut	Groton, CT
Vlahos	Penny	University of Connecticut	Groton, CT
Waddill	Dan	NAVFAC Atlantic	Norfolk, VA
Walker	Deborah	USACE Support Center, EM CX	Huntsville, AL
Woodley	Cheryl	NOAA National Ocean Services	Charleston, SC