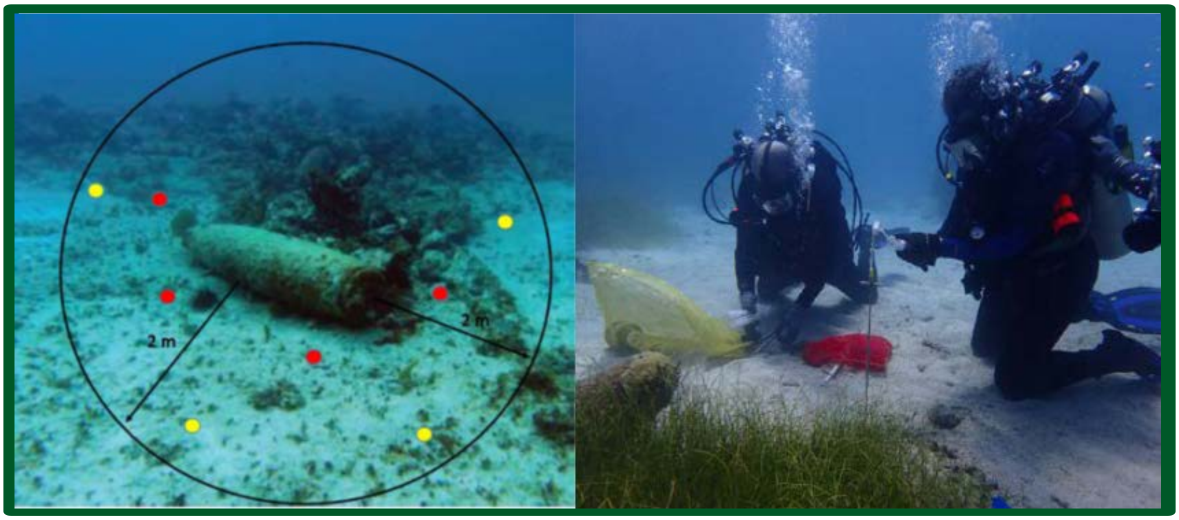
ESTCP
Cost and Performance Report

(ER-201433)



Validation of Passive Sampling Devices for Monitoring of Munitions Constituents in Underwater Environments

February 2018

This document has been cleared for public release; Distribution Statement A

ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Page Intentionally Left Blank

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
02/03/2018	ESTCP Cost & Perfromance Report	

4. TITLE AND SUBTITLE	
Validation of Passive Sampling Devices for Monitoring of Munitions Constituents in Underwater Environments	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	
Gunther Rosen, Robert George, William Wild: SPAWAR Systems Center Guilherme Lotufo, David Smith: ERDC Jason Belden: Oklahoma State University	5d. PROJECT NUMBER ER-201433
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
SPAWAR Systems Center 53475 Strothe Rd, Bldg. 111, Rm. 216 San Diego, CA 92152	ER-201433

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	
Environmental Security Technology Certification Program 4800 Mark Center Drive, Suite 17D03 Alexandria, VA 22350-3605	10. SPONSOR/MONITOR'S ACRONYM(S) ESTCP
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-201433

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A; unlimited public release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This demonstration focused on field validation of commercially-available passive sampling devices (PSDs), specifically Polar Organic Chemical Integrative Samplers (POCIS), that had recently been optimized for detection and quantification of MCs under environmentally-relevant conditions in laboratory-based studies (e.g., Belden et al. 2015). The DoD has custody and responsibility for human safety and environmental stewardship for coastal ranges, many of which have underwater sites that are known to contain underwater military munitions (UWMM), such as discarded military munitions (DMM) and unexploded ordnance (UXO), as a result of historic military activities.

15. SUBJECT TERMS

Passive Sampling Devices, Monitoring of Munitions Constituents, Underwater Environments

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Gunther Rosen
					19b. TELEPHONE NUMBER *(Include area code)*
UNCLASS	UNCLASS	UNCLASS	UNCLASS	62	619-553-0886

Page Intentionally Left Blank

COST & PERFORMANCE REPORT

Project: ER-201433

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

ACRONYMS AND ABBREVIATIONS

µg	microgram(s)
1,3-DNB	1,3-dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
BSS	Bahia Salina del Sur
CCP	Comprehensive Conservation Plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm	centimeter(s)
Comp B	Composition B (39.5% TNT, 59.5% RDX, 1% wax)
DMM	Discarded Military Munitions
DoD	U.S. Department of Defense
DOI	U.S. Department of Interior
EOD	Explosive Ordnance Disposal
ESTCP	Environmental Security Technology Certification Program
FUDS	Formerly Used Defense Site
GMI	Geo-Marine, Incorporated
GP	General Purpose
HC5	hazardous concentration values for 5% of species
HLB	hydrophilic-lipophilic balance
ISCO	*in situ* chemical oxidation
kg	kilogram
Kow	octanol-water partition coefficient
L	liter
lb	pound(s)
LIA	Live Impact Area
LIP	Leave in Place
LOD	Low Order Detonation
m	meter(s)
MC	munitions constituent
MDL	method detection limit
MR	munitions response

NAVFAC	Naval Facilities Engineering Command
NESDI	Navy Environmental Sustainability Development to Integration
ng	nanogram(s)
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOSSA	Naval Ordnance Safety and Security Activity
OSU	Oklahoma State University
PES	polyethersulfone
POCIS	Polar Organic Chemical Integrative Sampler
PSD	passive sampling device
QA	quality assurance
QC	quality control
QL	quantitation limit
RDX	hexahydro-1,3,5-trinitro-s-triazine (also Royal Demolition Explosive)
Rs	sampling rate
s	second
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Plan
SPE	solid-phase extraction
SSC	Space and Naval Warfare Systems Command (SPAWAR) Systems Center
TNT	2,4,6-trinitrotoluene
TWA	time-weighted average
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
UXO	unexploded ordnance
UWMM	underwater military munitions
VNTR	Vieques, Puerto Rico Naval Training Range

ACKNOWLEDGMENTS

This project was supported by the U.S. Department of Defense's Environmental Security Technology Certification Program (ESTCP), under project #ER-201433. Leveraged funding was provided by the Navy Environmental Sustainability Development to Integration (NESDI) program under Project #465. In-kind support for the field validation at Vieques, Puerto Rico Naval Training Range (VNTR) was provided by Naval Facilities Engineering Command (NAVFAC) Atlantic under the direction of Mr. Daniel Waddill (Head of Vieques Restoration Section), Kevin Cloe, Daniel Hood, and Madeline Rivera.

We gratefully acknowledge logistical and technical support from multiple organizations and individuals, including but not limited to Bart Chadwick (Space and Naval Warfare Systems Command [SPAWAR] Systems Center [SSC] Pacific); Nick Hayman and Jacob Munson-Decker (San Diego State University Research Foundation); Dr. Shane Morrison and Krystal Sieve (Oklahoma State University); Lauren Rabalais, Jim Biedenbach, and the analytical chemistry laboratory at the U.S. Army Engineer Research and Development Center (ERDC); Dr. Mace Barron, Jason Mangum, and team (U.S. Environmental Protection Agency Gulf Ecology Division laboratory in Gulf Breeze, FL); Dr. Stephen Fallis and Gregory Ostrom (Naval Air Warfare Center Weapons Division, China Lake); Diane Wehner (National Oceanic and Atmospheric Administration [NOAA] Office of Response and Restoration); and the CH2M HILL Munitions Response and Scientific Dive Teams.

Page Intentionally Left Blank

EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The U.S. Department of Defense (DoD) has custody and responsibility for human safety and environmental stewardship for coastal ranges, many of which have underwater sites that are known to contain underwater military munitions (UWMM), such as discarded military munitions (DMM) and unexploded ordnance (UXO), as a result of historic military activities. In addition to explosive blast (safety) considerations, regulators are increasingly concerned about potential ecological impacts of munitions constituents (MCs) on the marine environment, which has resulted in costly risk characterization efforts (e.g., NAVFAC 2011, USACE 2013, UH 2014a, UH 2014b) and could lead to more-resource-intensive remediation efforts. Accurate assessment of MC in underwater environments includes a high level of effort or difficulty required to (1) measure MC at very low (nanogram [ng]/liter [L]) concentrations; (2) identify leaking UWMM, and evaluate the nature of the leakage (e.g., varying levels of corrosion, MC release rates attenuated by currents, dissolution rate, biofouling, MC degradation); (3) measure MC release during episodic events; and (4) measure MC in biota in spite of low bioaccumulation potential (Lotufo et al. 2009, Lotufo et al. 2013).

This demonstration focused on field validation of commercially-available passive sampling devices (PSDs), specifically Polar Organic Chemical Integrative Samplers (POCIS), that had recently been optimized for detection and quantification of MCs under environmentally-relevant conditions in laboratory-based studies (e.g., Belden et al. 2015).

The technical objectives of the effort included the following Tasks:

Task 1: Conduct a controlled field validation study using a known source (i.e., fragments of the explosive fill material Composition B [Comp B]) placed in a marine environment;

Task 2: Conduct a calibration study to evaluate the performance of POCIS under multiple flow velocities and different levels of source material (e.g., shell) encapsulation, including fully-exposed versus breach-hole scenarios;

Task 3: Use the results from Tasks 1 and 2 to develop a technology user's guide for POCIS application at UWMM sites; and

Task 4: Conduct a full field validation study at a UWMM site, specifically a bay in the Live Impact Area at the Vieques, Puerto Rico Naval Training Range (VNTR).

Exposure data from the proposed validation efforts were then compared with existing toxicity criteria (Lotufo et al. 2017; SERDP 2017) to assess potential for ecological risk of UWMM associated with the data derived from the field. A technology user's guide is also appended to the Final Technical Report (Rosen et al. 2017).

TECHNOLOGY DESCRIPTION

The measurement of polar organic compounds in environmental matrices, especially at trace concentrations, represents a significant challenge. In recent years, significant improvements in analytical techniques coupled with the development of PSDs have much to offer towards *in situ* monitoring of ultra-low concentrations of emerging contaminants by providing a time-integrated sample with low detection limits and *in situ* extraction. PSDs are fairly well developed for legacy hydrophobic compounds (e.g., low density polyethylene membranes, polymer-coated jars or fibers) as well as for polar organic compounds (e.g., POCIS and Chemcatcher®).

The POCIS technology offers an advantageous alternative to traditional sampling methods (e.g., grab sampling) at sites where very low concentrations (ng/L) or fluctuation in concentrations are expected to occur, such as near underwater munitions. A continuous sampling approach allows detection and quantification of chemicals in an integrated manner, providing time-weighted average (TWA) concentrations, and the detection of chemicals that rapidly dissipate or degrade in the environment following release from the source (Alvarez et al. 2004, Mazzella et al. 2008). Unlike samplers that rapidly achieve equilibrium using very high surface area to sorbent volume, POCIS exhibits negligible loss rates and does not require a lengthy timeframe in order to reach equilibrium, allowing small masses of chemicals from episodic release events to be retained in the device by the end of the deployment period. The POCIS vastly simplifies sampling and preparation steps by elimination of electrical or fuel powering requirements, significantly reduces the numbers of analyses required, and provides protection of analytes against decomposition during transport and storage (Kot-Wasik et al. 2007).

DEMONSTRATION RESULTS

Performance was analyzed using a combination of quantitative and qualitative measurements to achieve the objectives of the project. The extent to which expected performance objectives were achieved was evaluated from the data collected in Tasks 1–3 and are elaborated upon in the report.

Performance Objective 1 was the verification that POCIS could detect MCs in a positive control field study at a clean site. Following permit approvals, 15 grams of Comp B (an explosive fill composed of 39.5% 2,4,6-trinitrotoluene [TNT], 59.5% hexahydro-1,3,5-trinitro-s-triazine [RDX], 1% wax) was placed at the site over a 13-day exposure. The performance objective was met, with POCIS-derived TNT and RDX average water concentrations ranging from 9–103 ng/L, with the highest concentrations within 0.3 meters (m) of the source. MC was non-detectable at stations >2 m from the source. Grab water samples collected and oyster tissues deployed at the site were below detection limits for all stations, indicating POCIS was the most sensitive technology for ultra-trace level detection in a controlled field study.

Performance Objective 2 was the verification that POCIS-derived TWA water concentrations and TWA concentrations derived from multiple grab sampling would produce similar results, or better results, for POCIS in a flume study simulating field conditions or in actual field studies. This objective was met for the Comp B flume study, the positive control field study, and the Vieques field validation study. Comp B flume-deployed POCIS estimated TWA water concentrations for TNT and RDX were similar to averaged concentrations generated using multiple grab TWA concentrations.

In the positive control field study, MC concentration was successfully determined using POCIS, while the discrete-sampling-derived concentrations as grab water samples resulted only in non-detects. In the Vieques field validation study, 1 of 30 sampling locations resulted in a relatively high water column concentration for TNT and several of its transformation products. The average TNT concentration from the two grab samples at the station was only 11% higher than the POCIS sample. The POCIS-derived average TNT concentration was 19% above the initial grab and 29% below the final grab sample concentration. POCIS-derived average RDX concentrations for 11 stations had detectable concentrations, while at the same locations only 3 stations had detectable concentration from grab samples during the initial period, and all stations were non-detect for the final period. Overall, data from grab samples validated the data obtained using POCIS for all the flume and field studies.

Performance Objective 3 was the demonstration of the effects of varying current velocities, in a series of controlled flume studies with precise velocity control, on the uptake of MC from spiked water to optimize sampling rates based on site-specific flow velocities. The objective was met, with a positive, statistically significant, linear relationship between current velocity and sampling rate for POCIS for multiple MC, providing useful means of applying appropriate sampling rates. From the regression equations derived, simple calculations are able to be used to correct for flow velocity if such measurements are made at the field site. In this project, a Nortek current profiler was used at Vieques to calculate the most accurate sampling rate based on measured flow. Two different explosive fill encapsulation scenarios showed highly comparable TWA concentrations for POCIS and average concentrations from multiple grab samples.

Performance Objective 4 was the demonstration that POCIS would detect MC at levels substantially lower than achievable using typical grab sampling methods. The quantitation limit (QL) for POCIS- derived TWA concentrations were consistently lower than those derived for discrete samples. Lower detection limits are achieved using POCIS sampling because the estimated volumes of water cleared of MC during the deployment time were substantially greater than the volume (1 L) consistently of all grab water samples. For the Comp B positive control study, the concentrations of TNT and RDX in grab samples were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 12 out of 20 stations. For 12 stations out of 15 in the Vieques field validation study, the concentrations of RDX in grab samples were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 8 out those 12 stations.

Performance Objective 5 was the demonstration of the success rate in terms of both recovery of POCIS from the field and the determination of useful data. A total of 20, 51, and 30 POCIS canisters (each containing 3 samplers) were deployed in the positive control field study, in the flume studies, and at the Vieques site, respectively. All samplers (100%) were recovered. Data were considered useful whether or not the concentrations were above or below method detection limits (MDLs), as it was expected that many field samples would be non-detect. All flume study data resulted in measurable concentrations, as the flume was spiked at concentrations to ensure detects. The strong correspondence between POCIS and multiple grab-based TWA concentrations in flume studies are a quantitative measure of the value of the POCIS data, showing negligible losses and post-uptake preservation of the parent compounds throughout the exposures.

Performance Objective 6 was the demonstration that all field and laboratory efforts followed experiment-specific quality assurance (QA) objectives and that quality control (QC) criteria were met. All criteria were met for this part of the project. Blanks, including field and laboratory, did not have MCs above the QLs. All spike tests had accuracy and relative precision within 25% of what was expected. In addition, all other sampling handling and instrument criteria were also met.

Performance Objective 7 was the demonstration of the ability to use POCIS TWA data for MC to evaluate ecological risk based on comparison with toxicity benchmarks developed from species sensitivity distributions. Compared to the high incidence of non-detects from grab samples, POCIS reported ≥ low ng/L MC concentrations in all tasks, allowing more quantitative assessment. Measured concentrations indicate negligible ecological risk based on comparison with hazardous concentrations derived from species sensitivity distributions. For Vieques, POCIS-derived TWA concentrations were 10–1,000,000 times lower than hazardous concentration values for 5% of species (HC5) generated from the most up-to-date and comprehensive species sensitivity distributions (SSD) as reported by Lotufo et al. (2017). Despite POCIS having a higher frequency of detection than grab samples at Vieques, detection levels for grab sampling and POCIS were below regulatory screening levels and both sampling methods showed no unacceptable risk. Therefore, the grab samples and POCIS are expected to be of equal value for Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) risk assessment at that site.

Performance Objective 8 was a qualitative objective of ease of operator use, requiring feedback from field and laboratory technicians on the usability of technology, sample prep and extraction, and time requirements. At Vieques, feedback in the field from Navy and contractor personnel was mixed. The deployment and recovery of POCIS went well, but the overall process was highly labor intensive, with dive teams and boat support required for both deployment and recovery of the samplers. The use of munitions response (MR) and scientific divers creates significant safety concerns associated with deployment and retrieval of POCIS. Overall, the level of effort and the associated safety concerns for POCIS are higher than grab sampling, which, if kept at a minimum, can be done in a single field effort without divers. Site managers understood the benefits of integrative sampling and the potential advantages of providing enhanced credibility through lower detection limits and obtaining data representative over extended timeframes, thereby sampling over a larger area. Grab sampling intended to provide temporal trends and TWA concentrations could require substantially more labor, depending on site-specific logistics and study objectives. Similarly, autosampling would require multiple trips to the site to obtain an integrated sample over time and ensure that MC do not degrade (e.g., freezing or extracting samples daily). Laboratory feedback indicated that processing of POCIS as compared to standard solid-phase extraction (SPE) of grab water samples was negligible.

Performance Objective 9 was the demonstration that the relative value of data from POCIS compared well with the cost of measurements from water and sediment porewater. POCIS was the only technology that detected MC at Gulf Breeze, FL, and had a higher frequency of detects compared to grab sampling at Vieques. The costs of using POCIS over more traditional means of water sampling (e.g., grab or composite sampling) are examined using multiple examples in the Cost Analysis section of the report, and suggest that POCIS are less expensive when traditional sampling involves multiple sampling events to develop an integrative sample (as opposed to single grab samples that would be less expensive than POCIS). However, for sites where regulatory requirements are for single grab samples, the costs for a POCIS-based program could be considerably higher.

Vieques is a complex site and the demonstration was designed to maximize the likelihood for detecting a leaking munition. It is unlikely that POCIS would be routinely applied in such a manner in a monitoring or regulatory program.

Performance Objective 10 was the qualitative objective of end-user understanding and acceptance of the POCIS technology for potential use at UWMM sites. Site managers and contractors understood the value of integrative samplers for MC and provided a considerable amount of in-kind support to successfully demonstrate the technology at Vieques. The notion that the use of POCIS would help with the criticisms of sampling at the wrong place and at the wrong time was seen as a primary advantage, especially considering the results of the Gulf Breeze study. Site managers on Vieques expressed concerns about the cost, diver safety, and difficulty of implementing POCIS. Site managers also noted that grab samples matched well with the POCIS results and the grab samplers are accepted by the regulators for risk assessment. Although the cost for POCIS is less than grab or composite sampling based on a sampling program that produced similarly integrative samples (see Section 7.0, Cost Assessment), the cost of collecting a single grab sample at a site would be less expensive than monitoring with POCIS.

IMPLEMENTATION ISSUES

Previous laboratory proof of concept and calibration and work for MC by this project team (e.g., Belden et al. 2015) and the demonstration and validation of POCIS in laboratory and field efforts for this project indicate the technology is highly valuable for assessment of MC exposure at UWMM sites. POCIS-derived TWA concentrations are expected to be more informative about exposure to MC compared to discrete grab samples when MC concentrations are low and MC is released to the water column in a time-varying nature, either from UWMM (Wang et al. 2013) or from terrestrial-based time varying inputs (e.g., runoff events or tidal pumping of groundwater contaminated with MC). For most applications, the cost associated with POCIS sampling is less than that for multiple grab or composite sampling required to represent a comparably integrated sample. In addition, POCIS sampling is expected to directly address sentiment from those concerned with (1) UWMM as sources of contamination and (2) who perceive grab sampling may take place at the wrong time and in the wrong place, and therefore (3) fail to adequately characterize exposure risk potential. UWMM site characterization using POCIS addresses all three of these concerns, and implementation as part of monitoring programs or for risk assessment should be considered depending on the site-specific objectives. Site characterization using POCIS may be site-wide or spatially focused or may be used to complement traditional sampling approaches to identify or rank sites of potential concern and support leave-in-place (LIP) versus removal decision-making processes.

CONCLUSION

Based on results from laboratory, positive field control, and UWMM site field validation efforts, the team concludes that POCIS is a valuable technology for characterizing MC contamination and assessing ecological risk at UWMM sites. A large number of published reports of field evaluations show that integrative sampling technology has been extremely useful for detecting a long list of hydrophilic contaminants when they might otherwise not be detected due to potential for time varying exposure and a requirement for low detection limits.

In this study, when detected, POCIS-derived RDX concentrations at Vieques ranged from 4–13 ng/L. POCIS-derived TNT concentration above the QL occurred at only 1 of 30 stations, with the relatively large value (5.3 microgram [µg]/L) quantified immediately adjacent to a breached munition. This said, even the highest MC concentrations observed in the field in this study were substantially lower than those expected to be hazardous to the most sensitive aquatic species and ecotoxicological endpoints. Identification of potentially breached bombs and projectiles by placing POCIS in close proximity to UWMM was conducted as part of this study to maximize the likelihood of success of demonstrating the technology at UWMM sites. However, such an approach is extremely labor intensive and expensive, and therefore, an unrealistic option as a sampling design for most site characterization and monitoring programs. The non-biased grid design used and described in this report, therefore, is expected to be more feasible than targeted sampling.

It should also be noted that the comparison of POCIS with grab sampling has several challenges in uncontrolled field settings, particularly if MC release or exposure is time-varying. However, increasing the volume of grab samples from 1 L to 10 L would more closely represent the volume cleared by the POCIS in a 2–3-week deployment and result in more comparable detection limits.

Finally, it should be noted that although POCIS data have the potential to be more informative as integrative samplers, the field validation at Vieques showed no ecological risk with either POCIS or traditional sampling technologies.

1. INTRODUCTION

1.1. BACKGROUND

The U.S. Department of Defense (DoD) has custody and responsibility for human safety and environmental stewardship for coastal ranges, many of which have underwater sites that are known to contain underwater military munitions (UWMM), such as discarded military munitions (DMM) and unexploded ordnance (UXO), as a result of historic military activities. In addition to explosive blast (safety) considerations, regulators are increasingly concerned about potential ecological impacts of munition constituents (MCs) on the marine environment, which has resulted in costly risk characterization efforts (e.g., NAVFAC 2011, USACE 2013, UH 2014a, UH 2014b) and could lead to more-resource-intensive remediation efforts. Although underwater UWMM have the potential to corrode, breach, and leak MCs, such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-s-triazine [RDX], and their major degradation products into aquatic environments (Lewis et al. 2009, Pascoe et al. 2010, Rosen and Lotufo 2010, Wang et al. 2013), a number of 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) measure MC at extremely low levels; (2) identify leaking UWMM, and evaluate the nature of the leakage (e.g., varying levels of corrosion, MC release rates attenuated by biofouling, MC biodegradation, MC photolysis, MC hydrolysis); (3) measure MC release during episodic events; and (4) measure MC in biota in spite of low bioaccumulation potential (Lotufo et al. 2009, Lotufo et al. 2013).

Passive sampling devices (PSDs), including Polar Organic Chemical Integrative Samplers (POCIS), show great promise for overcoming many of these challenges, with POCIS being the only known means for more efficiently characterizing MC concentration in water over time. The use of PSDs that generate time-weighted average (TWA) concentrations has provided tremendous cost savings in a diversity of monitoring programs (Miege et al. 2012). Integrative PSDs vastly simplify sampling and the sample preparation step by elimination of electrical or fuel powering requirements, significantly reducing numbers of analyses required, and providing protection of analytes against decomposition during transport and storage (Kot-Wasik et al. 2007). PSD data can subsequently be used to assess ecological exposure to MC based on propensity for uptake and toxicity to biota without having to make such measurements (Alvarez et al. 2012).

This project aimed to provide TWA MC concentrations at a UWMM site, providing valuable data to evaluate ecological risk associated with MC exposure to environmental receptors. Without such data, the DoD lacks methodological sensitivity and means for characterizing exposure at such sites, and would be unable to reduce the uncertainty associated with effectiveness of potentially unnecessary remedial actions, such as costly removal versus leave-in-place (LIP) options regardless of state of integrity or MC release.

1.2. OBJECTIVE OF THE DEMONSTRATION

This demonstration focused on field validation of commercially available PSDs, specifically POCIS, that had recently been optimized for detection and quantification of MCs at environmentally-relevant concentrations in laboratory-based studies under the Navy Environmental Sustainability Development to Integration (NESDI) program (Project #465).

The technical objectives of the effort included the following Tasks:

Task 1: Conduct a controlled field validation study using a known source (i.e., fragments of the explosive fill material Composition B [Comp B]) placed in a marine environment;

Task 2: Conduct a calibration study to evaluate the performance of POCIS under multiple flow velocities and different levels of source material (e.g., shell) encapsulation, including fully-exposed versus breach-hole scenarios;

Task 3: Use the results from Tasks 1 and 2 to develop a guidance document for POCIS application at UWMM sites; and

Task 4: Conduct a full field validation study at a UWMM site, specifically a bay in the Live Impact Area at the Vieques, Puerto Rico Naval Training Range (VNTR).

Exposure data from the proposed validation efforts were then compared with existing toxicity criteria (Lotufo et al. 2017, SERDP 2017) to assess the potential for ecological risk of UWMM associated with the data derived from the field. A technology user's guide intended for use by DoD end users, regulators, and commercial laboratories is included as part of the Final Technical Report (Rosen et al. 2017) and is available on the Environmental Security Technology Certification Program (ESTCP) website.

1.3. REGULATORY DRIVERS

In the United States, UXO and DMM are present at sites designated for Base Realignment and Closure (BRAC), at Formerly Used Defense Sites (FUDS), and at operational military ranges. Within the FUDS program, the U.S. Army Corps of Engineers (USACE) has identified >400 sites, totaling >10 million acres that potentially contain munitions in underwater environments. The U.S. Navy and U.S. Marine Corps Munitions Response Program (MRP) have identified an additional 37 sites containing underwater munitions (Bryan Harre, MRP, pers. comm.). The inventory includes sites that date back to the 18^{th} century and some that were used as recently as the 1990s (SERDP 2010).

Regulatory concern at these sites stems from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and U.S. Environmental Policy Act (USEPA) requirements to protect both human health/safety and environmental quality. Efforts to date to assess underwater ecological risk associated with MC are scarce. For example, concerns about marine tissue concentrations at Jackson Park (Bremerton, WA) (NAVFAC 2011) have largely been unresolved due to insufficient clarity regarding analytical sensitivity to detect potentially toxic MC. Therefore, it is believed that munitions response (MR) sites will gain critically valuable information for making scientifically defensible risk management decisions at these sites, which will assist with remedial mitigation options such as LIP, low order detonation (LOD) versus removal, or blow in place (BIP).

Drivers Specific to Vieques, Puerto Rico. Since Vieques is a Superfund site, the regulatory drivers for addressing MC underwater at Vieques are the CERCLA-based screening levels. The highest MC concentrations observed in field studies are substantially lower than screening levels. Therefore, MC concentrations are not expected to create unacceptable risk in the underwater environment of Vieques, and MC is not expected to drive underwater cleanup of munitions at Vieques.

2. TECHNOLOGY

2.1. TECHNOLOGY DESCRIPTION

The measurement of polar organic compounds in environmental matrices, especially at trace concentrations, represents a significant challenge. In recent years, significant improvements in analytical techniques coupled with the development of PSDs have much to offer towards *in situ* monitoring of ultra-low concentrations of emerging contaminants by providing a time-integrated sample with low detection limits and *in situ* extraction. PSDs are fairly well developed for legacy hydrophobic compounds (e.g., low density polyethylene membranes, polymer-coated jars or fibers) as well as for polar organic compounds (e.g., POCIS and Chemcatcher®).

Figure 2-1. POCIS Sampler (left) and Commercially-available Field Holder and Canister for POCIS (right).

The POCIS technology (Figure 2-1) offers an advantageous alternative to traditional sampling methods (e.g., grab sampling) at sites where extremely low-level concentrations or fluctuation in concentrations are expected to occur, such as near underwater munitions. A continuous sampling approach allows detection and quantification of chemicals in an integrated manner, providing TWA concentrations, and the detection of chemicals that rapidly dissipate or degrade in the environment following release from the source (Alvarez et al. 2004, Mazzella et al. 2008). Unlike samplers that rapidly achieve equilibrium using very high surface area to sorbent volume, POCIS exhibits negligible loss rates and does not require long times to reach equilibrium, allowing small masses of chemicals from episodic release events to be retained in the device by the end of the deployment period. The POCIS vastly simplifies sampling and preparation steps by elimination of electrical or fuel powering requirements, significantly reduces the numbers of analyses required, and provides protection of analytes against decomposition during transport and storage (Kot-Wasik et al. 2007).

The POCIS was developed to sample a wide variety of organic compounds with log octanol-water partition coefficient (K_{ow}) of ≤4. Because TNT, RDX, and their major degradation products have relatively low log K_{ow} values (of approximately ≤2), and because the POCIS has been successfully used in marine environments (Harman et al. 2012, Munaron et al. 2012), this sampling technology was considered potentially suitable for estimating TWA concentrations of explosives at UWMM sites, which was verified in laboratory-based calibration experiments under the NESDI program, Project #465. The POCIS consists of a receiving phase (sorbent) sandwiched between two polyethersulfone (PES) microporous membranes with ~0.1 micrometer (μm) pore size (Alvarez et al. 2004, see Figure 2-2). The sampler is compressed using two stainless steel rings (interior diameter

51–54 millimeter [mm]), which provides an exposure surface area of 41–46 square centimeters (cm^2). The samplers are available commercially from Environmental Sampling Technologies (EST), which use the widely used Oasis® hydrophilic-lipophilic balance (HLB) sorbent.

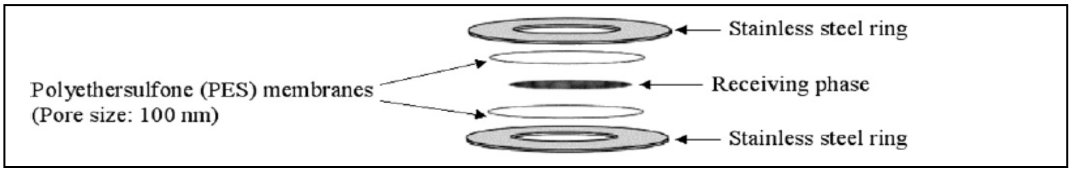


Figure 2-2. Disassembled View of the POCIS (from Morin et al. 2012).

The sampling rate (R_s) is defined as the volume of water cleared in a unit of time for a given molecule type, and is required for the determination of the TWA concentration for different chemicals from POCIS. Despite some attempts to correlate POCIS R_s with some physicochemical property of grouped target compounds such as log K_{ow} (e.g., Li et al. 2010, Mazzella et al. 2008), an overall model is lacking. Therefore, uptake rates must be empirically calibrated.

A multitude of factors affect sampling rate, thus the accuracy of calibration sampling rates in subsequent environmental studies is dependent on how similar the site exposure conditions are to those used in the calibration experiment (Harman et al. 2012). The pattern and rate of water flow (i.e., current velocity and direction) across the PES membranes that house the POCIS sorbent generally have the largest impact on R_s. This is because diffusion of dissolved substances across the membrane is dependent on the thickness of the water boundary layer at the membrane surface, and is affected by water flow/turbulence around the sampler (as reviewed by Harman et al. 2012 and Morin et al. 2012). On a relative scale, other variables, including temperature, nutrients, dissolved organic carbon, salinity, and biofouling, typically have less impact on R_s.

A generalized example of the use of the samplers is shown in Figure 2-3, while a summary of the evolution of the technology is provided in Figure 2-4.

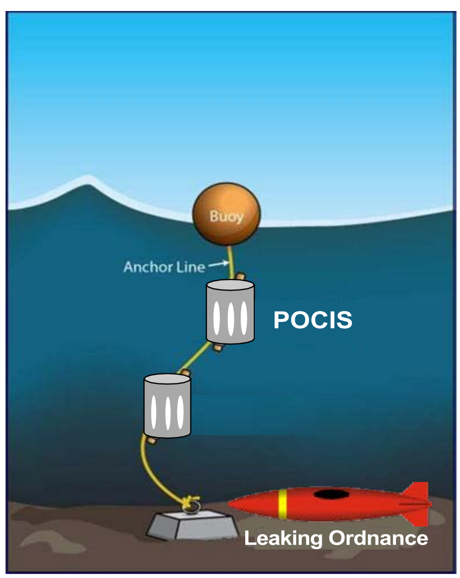


Figure 2-3. Generalized Diagram of How POCIS Might Be Incorporated into Site Characterization at a UWMM Site.

- US Patent 6,478,961 B2 (Petty et al., 2002)
- Commercially available from EST, Inc., for pharmaceuticals and polar pesticides (2003)
- USGS POCIS Guidance (Alvarez, 2010)
- Critical review papers (Harman et al. 2012; Morin et al. 2012)
- NESDI Project #465: Calibration/lab demo for Munitions Constituents (MC; 2011-14)
- Positive control field validation for MC, Santa Rosa Sound, FL (Rosen et al., 2014)
- Publication of NESDI project MC results (Belden et al 2015)
- Refinement of sampling rate for MC (ESTCP ER-201433, current project)

Figure 2-4. Chronological Summary of the POCIS Technology to Date.

Tasks 1 and 2 of this project involved meaningful technology field validation and laboratory-based refinement prior to the full-scale field validation at Vieques. A brief overview of these studies is provided here, and shown in full in Appendices of the Final Technical Report (Rosen et al. 2017).

Positive Control Field Study. POCIS were deployed at varying distances from fragments of the explosive formulation Comp B (39.5% TNT, 59.5% RDX, and 1% wax binder) in an embayment of Santa Rosa Sound (FL). POCIS-derived TWA water concentrations from a 13-day deployment ranged from 9–103 nanograms (ng)/L for TNT and RDX outside the source canister, with concentrations decreasing with increasing distance from the source to below quantitation limits (QLs) (5–7 ng/L) at stations >2 meters (m) away from the source. The study verified the sensitivity of the samplers when a known quantity of explosive fill is present. The study was followed by a biofouling study to assess potential impacts of biofouling on sampling rate. The results of this study are recently publicly available (Rosen et al. 2018).

Spiked Flume Studies. The primary objective of these studies (Task 2) was to evaluate MC uptake rates by POCIS under precision-controlled flow velocities inside a large (30,000 gallon) flume. In addition to investigating the influence of flow rate (range 7–30 centimeters [cm]/second [s]) on POCIS R_s, the team evaluated the influence of location in the flume, orientation of the POCIS relative to the flow, and the presence/absence of the protective canister on sampling rate. These efforts resulted in regression equations that allow accurate TWA concentration estimation when flow at the field site is known. As expected, flow rate had a significant effect ($p < 0.01$) on R_s for every MC evaluated for both uncaged and caged POCIS. For the range of flow rates examined here, sampling rate increased linearly for all MC investigated with a strong fit (r^2=0.79–0.98) for TNT and DNTs, but with a weaker fit (r^2=0.46 and 0.53, uncaged and caged, respectively) for RDX. The results of these studies are recently publicly available (Lotufo et al., 2018).

Comp B Flume Studies. To further evaluate the ability of POCIS to capture slowly-increasing MC concentrations to accurately estimate a TWA concentration, experiments were conducted in the flume using two realistic exposure scenarios: scenario 1 representing the release of MC from fully exposed Comp B fill, simulating an LOD, and scenario 2 representing the release of MC from Comp B through a small hole, simulating a recently breached munition. In both scenarios, the release of MC into the flume water was quantified using a combination of POCIS and frequent grab sampling for each experiment duration (10-day for the exposed fill experiment and 13-day for the hole experiment).

These studies showed negligible differences between MC uptake by caged and exposed POCIS samplers, and showed minimal differences between POCIS and multiple grab-derived TWA concentrations for TNT and RDX. The release of MC under the scenarios described above was also estimated in the context of the Shell model (Wang et al. 2013), which was developed to estimate the mass of MC introduced into the surrounding aquatic environment from a single breached munition casing or dispersed by an LOD, among other scenarios.

2.2. ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.2.1. Advantages

The POCIS provide high sensitivity (i.e., low detection limits) and continuous, integrative, sampling capability. These are substantial advantages over discrete grab sampling, or automated sampling (for which relatively large volumes of water would be required to be collected), especially for UWMM sites where MC exposure might be episodic (e.g., terrestrial runoff, groundwater seepage, breached munition release rate dynamics). The samplers also protect adsorbed contaminants against degradation, which could otherwise occur in water samples. POCIS are highly demonstrated, have been calibrated for >300 different polar organic chemicals, and are commercially available. POCIS are also simple to deploy, are relatively inexpensive, and can be easily analyzed by commercial laboratories. The ability to detect MC at UWMM sites, while other methods are likely to yield non-detects, is expected to be extremely valuable for improving the determination of environmentally-relevant MC concentrations and will assist tremendously with calculations of ecological risk associated with MC at such sites.

2.2.2. Limitations

One of the primary limitations of POCIS is that they are generally considered semi-quantitative (e.g., Bueno et al. 2016). The contaminant-specific *Rs* used towards the estimation of a TWA concentration by POCIS is dependent on a variety of *in situ* exposure conditions including current velocity, salinity, pH, temperature, dissolved organic compounds, and biofouling. That said, most of these variables appear to have overall minimal effect on *R* (Harman et al. 2012). Efforts to improve the quantitative ability of POCIS are ongoing, including a recently completed Strategic Environmental Research and Development Plan (SERDP) Exploratory Development (SEED) project (SERDP 2016) that reported clear advantages towards the use of nylon mesh to reduce the influence of flow on MC uptake or the incorporation of microflow sensors into the exposure canister for precise *in situ* current measurements, which in turn could be used for the selection of *Rs* that allow the calculation of accurate TWA concentrations. Current velocity was also investigated in this project, and regression equations were developed to correct for velocity if current meters are incorporated into the field test design with POCIS. With respect to UWMM sites in deep water or high energy environments, costs and safety considerations associated with the requirement of highly-skilled dive teams may be required for successful execution.

3. PERFORMANCE OBJECTIVES

The Performance Objectives for this study are divided into quantitative objectives (objectives that were measured against a standard or set criteria to demonstrate success) and qualitative objectives (objectives that required a particular observation during use of the technology or in the end result). Performance Objectives are shown in Table 3-1.

Table 3-1. Performance Objectives for the Demonstration of POCIS Technology.

	Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives				
1	POCIS will detect MC in positive control field deployment (Gulf Breeze, FL).	In controlled field study, POCIS analyzed for TNT, aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs), and RDX.	Detectable MC concentrations in POCIS.	**Met.** In controlled field study with Comp B explosive fill material, MC detected at 9–103 ng/L 0.3–2 m from source.
2	POCIS will accurately quantify time-averaged MC concentrations in the water column.	Simultaneous collection of POCIS-derived and discrete-sampling-derived concentrations under actual field conditions or field conditions simulated in a flume.	For flume study simulating field conditions and for the positive control and the Vieques field studies, POCIS estimated TWA concentrations validated using concentrations determined for grab water samples.	**Met.** Comp B flume studies showed POCIS TWA concentrations similar to TWA concentrations derived for multiple grab samples. In the positive control field study, POCIS-MC data were detected at low ng/L concentrations in a gradient from the source, but grab samples were always non-detect. In the Vieques field validation, detected TNT concentrations were similar (within 11%) when comparing grab samples with POCIS.
3	POCIS will quantify MC under different flow velocities and MC release conditions.	Sampler uptake data among varying flow velocities in flume.	Development of sampling rates and TWA concentrations under controlled experimental conditions in a flume.	**Met.** A positive linear relationship between flow velocity and sampling rate for POCIS was established for multiple MC, useful for correcting sampling rate based on flow velocity. Two different explosive fill encapsulation scenarios showed highly comparable TWA concentrations for POCIS and multiple grab samples.

Table 3-1. Performance Objectives for the Demonstration of POCIS Technology. (Continued)

	Performance Objective	Data Requirements	Success Criteria	Results
4	POCIS sampler will detect MC at levels substantially lower than detection limits achievable for grab samples.	Conduct field and flume studies using discrete (i.e., grab) sampling alongside integrative POCIS samplers.	1) QL for POCIS substantially lower than QL for discrete water samples. 2) POCIS continuous sampling over time will result in MC detection while MC in corresponding discrete water samples below detection. 3) POCIS continuous sampling over time at field sites will result in higher frequency of detection of MC compared to grab samples.	1) **Met.** The QL for POCIS-derived TWA concentrations were consistently lower than those derived for discrete samples. 2) **Met**. For the positive control study, TNT and RDX in all grab samples reported as non-detects with detects obtained for 12 of 20 POCIS stations. For 12 of 15 stations at Vieques, RDX in grab samples reported as non-detects while POCIS detected RDX at 8 of those stations. 3) **Met.** For the positive control study, TNT and RDX from grab samples had a detection frequency of 0%; contrastingly, POCIS-derived TWA concentrations were detected at a rate of 60%. For Vieques field validation, RDX in initial grab samples had a detection frequency of 20%, while for final grab samples RDX was reported as non-detect for all stations. Contrastingly, POCIS had a detection frequency of 79%.
5	POCIS will successfully detect MC concentration at a site (Success Rate).	Useful POCIS, water, sediment, and tissue data from target sampling locations.	Useful data collected for at least 80% of locations for POCIS.	**Met**. 100% of samplers were recovered from positive control, flume, and Vieques field efforts. 97% of Vieques POCIS produced useful data (1 sample lost in laboratory).
6	Quality control (QC) and quality assurance (QA) meet technology requirements.	Site- and/or experiment-specific sampling and analysis plans (e.g., demonstration plan) will be developed.	As defined in the sampling and analysis plans, to include trip and laboratory blanks less than QL, laboratory spikes within 25% of expected, chain of custody and sample control procedures followed for all samples.	**Mostly Met.** Trip blanks and laboratory blanks were below QLs. All chain of custody and sample control procedures were met. Extraction of POCIS and solid-phase extraction (SPE) of water samples were <25%. A few analytes in tissue and sediment had recoveries up to 30% lower. See Appendix E of the Final Technical Report (Rosen et al. 2017) for more details.

Table 3-1. Performance Objectives for the Demonstration of POCIS Technology. (Continued)

	Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives				
7	UWMM field validation	POCIS will provide useful data for assessing potential MC exposure at underwater UXO sites.	Reporting of MC at low enough concentrations to determine realistic assessment of ecological risk.	**Met.** Instead of largely non-detects from grab samples, POCIS reported ≥ low ng/L MC concentrations in all tasks, allowing more quantitative assessment, but negligible ecological risk based on species sensitivity distributions.
8	Ease of use	Feedback from field deployment personnel and laboratory technicians on usability of technology, sample preparation and extraction, and time requirements.	Reduced effort relative to traditional sediment and water chemical sampling and analysis.	**Met**. Feedback in field by DoD contractors was mixed. Contractors indicated the deployment and recovery went well, but noted the design was labor intensive, and costly in comparison to grab sampling, which can be done in a single field effort without divers. The team agrees with this conclusion if integrated sampling does not provide added value, but complexity is comparable if autosampling and multiple trips to the site are desired for an integrated sample.
9	Cost-benefit	Costs for acquiring data, and usefulness of data via comparison of POCIS, water, and sediment.	Relative value of data compared to cost of traditional measurements from water, sediment, and tissues.	**Met.** POCIS was the only technology that detected MC in a positive control study and had a higher frequency of detects compared to grab sampling at Vieques. It is noted, however, that in this case, both POCIS and grab samples were below regulatory screening levels, with both clearly showing no unacceptable risk. The high percentage of detections with POCIS may show the Vieques public that samplers were placed in representative locations.
10	End user understanding and acceptance	Feedback from end users including site managers and regulators from reports, webinars, meetings.	Positive feedback and consideration of integration of the technology in assessments at MR sites.	**Met.** Site managers and contractors understood value of integrative samplers and provided considerable in-kind support to successfully demonstrate the technology at Vieques. Concerns were expressed about cost, diver safety, and regulatory acceptance at their sites.

Page Intentionally Left Blank

4. SITE DESCRIPTION

4.1. SITE LOCATION AND HISTORY

During the 1940s, the U.S. Navy purchased 25,000 acres of land on Vieques Island, Puerto Rico, on the eastern and western ends of the island. The acquired land was used for Naval gunfire support and air-to-ground training from the 1940s until 2003. The former VNTR is located on the eastern half of the island. Comprising approximately 14,573 acres, the VNTR provided ground warfare and amphibious training for the U.S. Marine Corps, naval gunfire support training, and air-to-ground training. The former VNTR was divided into four separate operational areas, comprising from west to east: the Eastern Maneuver Area (EMA), the Surface Impact Area (SIA), the Live Impact Area (LIA), and the Eastern Conservation Area (ECA) at the easternmost tip of the island.

On April 30, 2003, the former VNTR was transferred to the U.S. Department of the Interior (DOI) to be operated and managed by the U.S. Fish and Wildlife Service (USFWS) as a National Wildlife Refuge pursuant to Section 1049 of the National Defense Authorization Act for Fiscal Year 2002 (Public Law 107–107). Approximately 900 acres of the former VNTR, consisting of the LIA, is managed as a wilderness area where public access is prohibited. DOI developed a Comprehensive Conservation Plan (CCP) in 2007 for the Vieques National Wildlife Refuge that outlines its concept for managing the refuge. Environmental restoration of the former VNTR is based on potential risks to human health and the environment identified via the CERCLA process, together with applicable or relevant and appropriate requirements (ARARs), with consideration given to the future land use identified in the CCP (CH2M HILL 2013).

The Bahia Salina del Sur (BSS) is an embayment on the southeastern shoreline of the LIA that is adjacent to a mock airstrip and several targets, which resulted in high densities of UWMM (GMI 2007, McDonald 2009), and is the focus for this technology demonstration.

4.2. SITE GEOLOGY/HYDROLOGY

The BSS covers approximately ¾–½ nautical miles with water depths up to slightly more than 30 feet (Bauer et al. 2010). The bottom of the bay consists of areas of open sand, areas covered by marine sea grasses, and coral reefs. The coral tend to be located in fringing clusters around islands and along the shoreline. Areas of coral in the main part of the bay are typically associated with solid bottom structures (such as the components of the wrecked ex-*USS KILLEN* (a U.S. Navy target ship; Deslarzes et al. 2002) or piles of dead coral rubble (likely created by earlier ordnance detonations). The entire island of Vieques has its origins in volcanic activity. There are hills, rugged terrain, and rocky outcroppings at various places on Vieques that demonstrate its volcanic origins (McDonald 2009).

The vast majority of the sea bottom in BSS is sand, with <10% coral cover, but significant seagrass can be present ranging from patchy (10–90%) to continuous (90–100%) in some areas (Bauer et al. 2010). The nearshore currents around Vieques are influenced by both the prevailing trade winds and tidal flow. The longshore surface currents to the north and south of the island flow in an east/northeast to west/southwest direction at approximately 10 cm/s (GMI 2003).

Prevailing current velocities during the demonstration were measured on orders of minutes to hours at several of the sampling locations as this information is helpful for enhanced calculation of the TWA concentration with the POCIS technology. Capella et al. (2003) also documented a west/southwest circulation pattern in the region north of Vieques. Flood and ebb tidal currents vary in speed and direction around different portions of the island (GMI 2003). North of Vieques, between Vieques and Culebra, reported typical tidal flow peaks were 10–20 cm/s in the region with a mean vector velocity of 5 cm/s (Capella et al. 2003).

4.3. CONTAMINANT DISTRIBUTION

MC concentrations at Vieques. Few data are available to sufficiently characterize the extent and magnitude of MC concentrations in sediment or water at Vieques. A National Oceanic and Atmospheric Administration (NOAA) study involving 78 sediment samples encompassing analysis of 15 energetics and related compounds reported inconclusive evidence of presence of any energetics (Pait et al. 2010). Similarly, CH2M HILL (2007) detected no energetics in 79 soil samples collected in the VNTR, while NOAA and Ridolfi (2006) detected no energetics in crab tissue samples in 12 locations across Vieques. ATSDR (2006), however, reported 0.97 µg/gram (g) HMX in fiddler crab (*Uca sp.*) tissues taken in the former LIA. Porter et al. (2011) reported various MC in water, sediment, and biota sampled at BSS, most samples taken adjacent to an unexploded, breached 2,000-pound (lb) bomb near the ex-*USS KILLEN* stern, representing the only underwater detection of MC at Vieques reported to date.

Munitions surveys at BSS. The documented presence of underwater UXO at BSS was one of the primary reasons for selection of this site for demonstrating the POCIS technology. The most comprehensive evidence available at the time of writing the project demonstration plan included that from (1) a near-shore survey focused adjacent to military targets T1–T6 (GMI 2007); (2) a NOAA survey with Geo-Marine, Inc. (GMI) ground-truthing in the central part of BSS (GMI 2007); (3) a U.S. Navy survey primarily along the northern shoreline (unpublished data); and (4) coordinates from historical collection of U.S. Navy water hits from >10 years of observations from gun fire along the southeast coastline of BSS.

5. TEST DESIGN

5.1. CONCEPTUAL EXPERIMENTAL DESIGN

Earlier project tasks included validation that POCIS was sufficiently sensitive to detect estimated low part-per-trillion (ng/L) TWA MC water concentrations in a known source field study at Gulf Breeze, FL (Task 1), and optimization of sampling rates for different flow velocities (Task 2). The remainder of performance objectives associated with the technology demonstration were addressed by a full-scale deployment at BSS, a known Navy MR site with significant quantities of UWMM previously documented (GMI 2007). A conceptual diagram of the basic experimental design at BSS is shown in Figure 5-1.

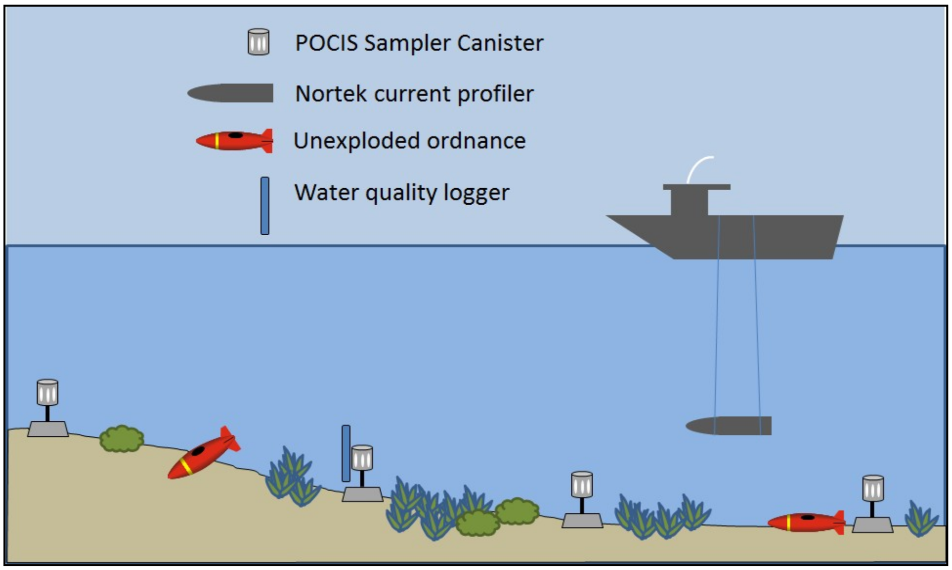


Figure 5-1. Generalized Experimental Approach for the Technology Demonstration at BSS.

The generalized experimental design at BSS included two strategies for POCIS deployment: (1) a non-biased (Grid) deployment of POCIS equally spaced over the majority of the bay using a grid design, and (2) a biased (Targeted) deployment of POCIS placed immediately adjacent to munitions following visual inspection and MR diver opinion regarding likelihood for containing, and potentially leaking, MCs (Figure 5-2). The rationale for the Grid approach was to assess the technology's value as a screening tool to identify any MC presence, and magnitude of concentration across a UWMM site known or suspected to contain UWMM, but with limited or no knowledge of presence or condition of munitions. The Targeted approach aimed to sample munitions that were suspected of releasing MC into the water column via dissolution of explosive fill material following corrosion or a physical breach of the metallic housing. It should be noted, however, that it was beyond the scope of this project to positively verify that munitions selected for the Targeted approach were indeed releasing MCs prior to the POCIS demonstration due to the complexities associated with verification of such a scenario, and Naval Ordnance Safety and Security Activity (NOSSA) regulations that required no direct contact with the UWMM.

Magnitude and frequency of detected MC at sites using the TWA concentrations derived from POCIS were compared with those from grab samples collected during the deployment and recovery, and ultimately compared with aquatic toxicity screening values for MC, including water quality criteria and hazardous concentrations derived from species sensitivity distributions (Lotufo et al. 2017; SERDP 2017).

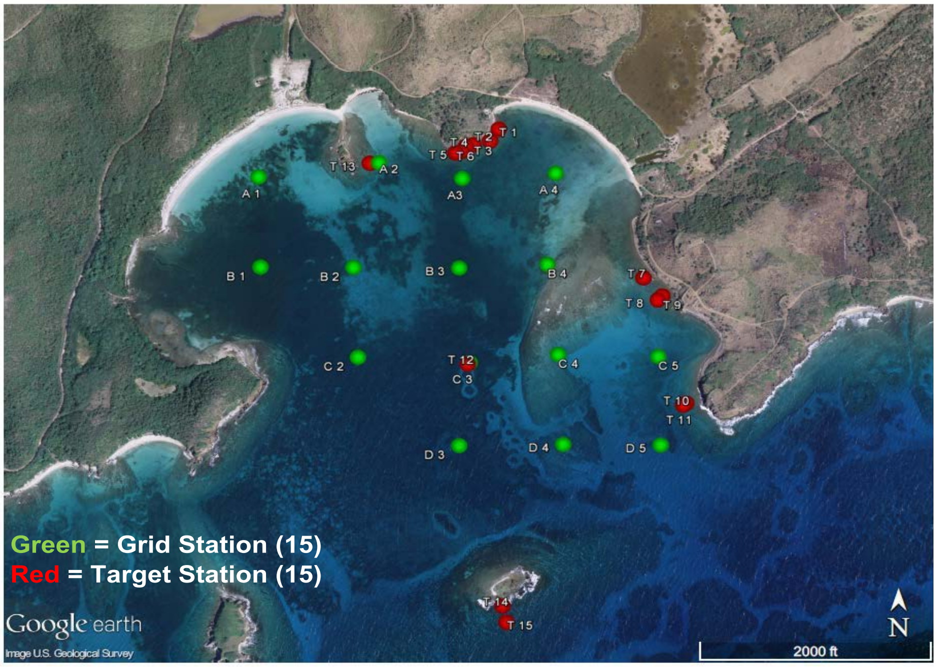


Figure 5-2. Deployment Locations of Grid and Target POCIS Deployments.

5.2. BASELINE CHARACTERIZATION

Baseline characterization associated with this site demonstration relied on a combination of previous ground-truthing of magnetic anomalies (i.e., detections) already performed by dive surveys subsequent to geophysical surveys (GMI 2007), and critical visual inspection of candidate munitions immediately prior to this POCIS technology demonstration. With oversight provided by the Naval Facilities Engineering Command (NAVFAC) Atlantic, CH2M HILL MR divers conducted a reconnaissance survey in early January 2016 to support this demonstration. The MR divers identified and photo-documented 25 candidate items, largely located along the northern and eastern shorelines of BSS, for discussion with the project team. These were a combination of Mk-series bombs and a variety of projectiles across a range of degrees of corrosion. The ESTCP project team selected 15 of these items, based on detailed discussion with the MR dive team, for the POCIS deployment.

5.3. LABORATORY STUDY RESULTS

A series of flume experiments were conducted by the project team to optimize the calculation of *Rs* for multiple MC under site-specific flow velocities. This was pursued due to flow current velocity being one of the primary parameters creating uncertainty associated with accurate estimation of the TWA concentration. The details of these studies are provided in Appendices C and D of the Final Technical Report (Rosen et al. 2017).

5.4. DESIGNS AND LAYOUT OF TECHNOLOGY COMPONENTS

POCIS canisters (each containing 3 samplers) were positioned approximately 12 inches above the sea floor. Target (i.e., adjacent to munitions) stations used a weighted-block system (Figure 5-3) weighing approximately 45 lb and carefully placed by the item in a secure location by MR divers with the assistance of a lift bag. Because Grid stations could be safely cleared to NOSSA requirements using a magnetometer, 36-inch sand screws were used to securely anchor POCIS canisters used at these stations (Figure 5-4). The deployment approach was fully vetted by Navy Explosive Ordnance Disposal (EOD), NOSSA, NOAA, and the National Marine Fisheries Service (NMFS) based on both safety and ecological considerations. All deployed equipment was removed during the recovery operation.

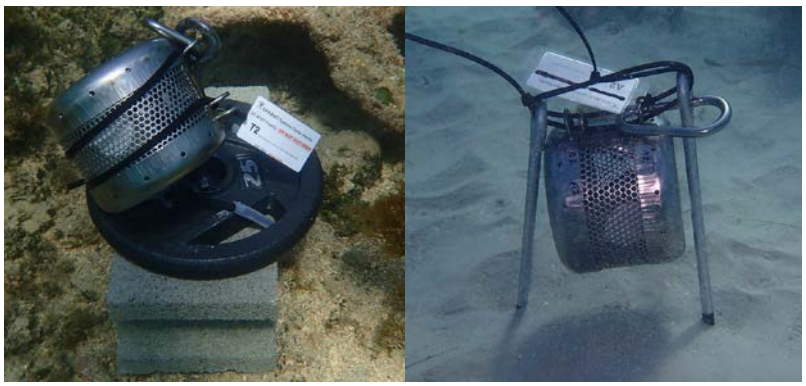


Figure 5-3. Weighted-block System (left) Used for Placement of POCIS Adjacent to Targeted Munitions and Sand Screws (right) Used to Place Sampling Canister at Grid Stations.

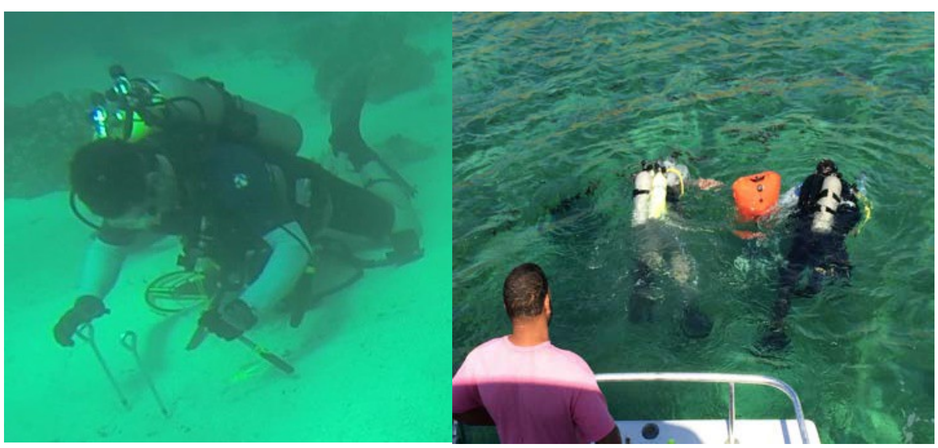


Figure 5-4. Sand Screws Were Used to Secure Grid Stations to Sea Floor After Clearance with a Magnetometer (left). Lift Bags Were Used to Transport the Weighted Block System Used to Position POCIS Canisters within 12 Inches of Target Munitions (right).

5.5. FIELD TESTING

Based on the relatively simple nature of the technology, no major installation efforts were required, minimizing the need for time, equipment, and personnel requirements at the site. The vast majority of the field time involved access to and from the site and diver safety considerations (e.g., compliance with strict MR diver procedures) while onsite.

In brief, there were five significant phases of the demonstration (occurring December 2015–July 2016), including: (1) site-specific anchoring trial, (2) reconnaissance study to select candidate munitions, (3) technology component deployment (three field days), (4) technology component recovery (three field days), followed by (5) a one-time focused verification sampling effort of porewater and sediment (two field days) based on results from phases 1 and 2. The schedule for the technology demonstration is summarized in the Final Technical Report (Rosen et al. 2017).

5.5.1. POCIS Grid Deployment

A total of 15 POCIS canisters (each containing three HLB POCIS) were deployed at the test site using a non-biased grid design that encompassed the majority of the Bahia (Figure 5-2). The total area of the grid is ~10^6 square meters (m^2) (~250 acres), with individual sampling canisters approximately 250 m apart. While the Grid stations were deployed using installation of 36-inch sand screws following verification of no hazard using a magnetometer in a 25-foot radius, the weight-block system used for placement at Target stations was installed by transport of the assembly to the station using lift bags (Figure 5-4).

5.5.2. POCIS Targeted Deployment

A second set of 15 POCIS canisters were deployed adjacent to munitions for which visual inspection suggested potential for exposed and potentially leaking MC. These items were identified during the reconnaissance survey led by NAVFAC personnel and CH2M HILL dive teams a few days prior to sampler installation. The dive teams used historical knowledge of the site (see Section 4.1) and the project team's objectives/input to locate and rank a variety of items. Ranking of the items was based on a number of factors including:

- Likelihood to potentially contain explosive fill material
- Representation of different munition types (e.g., various sized projectiles and bombs)
- Condition (i.e., level of corrosion and observed breaches)
- Requirement for safe access and placement of sampler adjacent to the item.

The Final Technical Report (Rosen et al. 2017) shows locations (including coordinates and photographs) where Grid and Target samplers were deployed, along with descriptors of munition type, condition, depth, and/or substrate at each sampling location. Representative target munition sampler placement is shown in Figure 5-5.

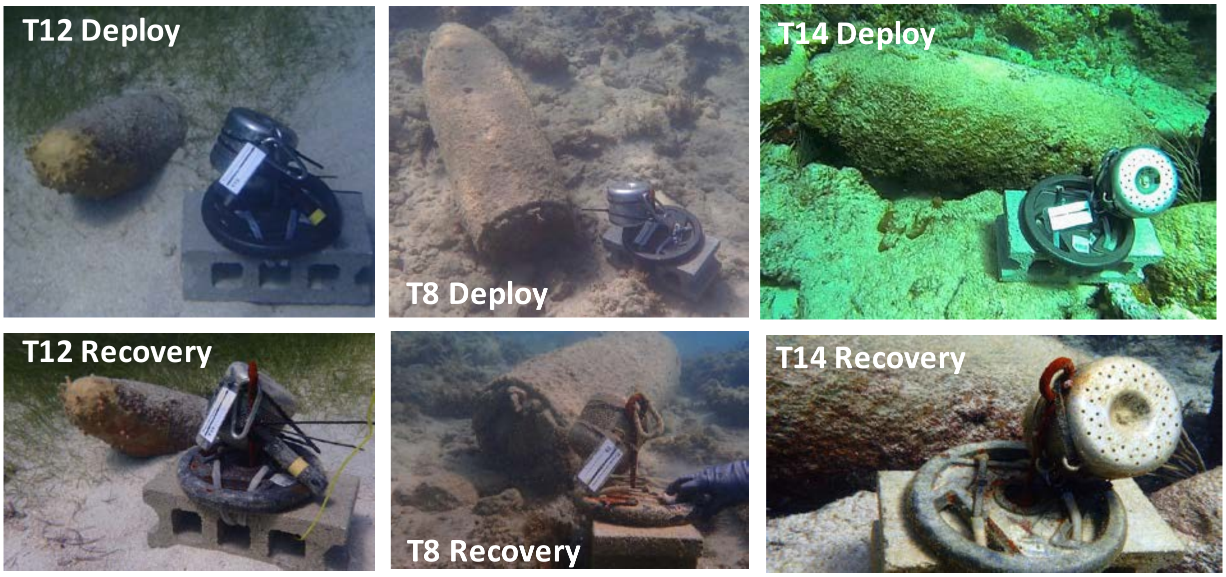


Figure 5-5. Representative Target Items and POCIS on Deployment (top) and On Recovery (below) After Approximately Three Weeks.

5.5.3. Discrete Water Sampling for MC

Water was sampled by two means: POCIS and discrete grab samples. POCIS were used to derive estimated TWA water concentrations as already described. A 19–23-day POCIS exposure (station-dependent, based on time required to deploy and recover samplers over a 3-day period each) occurred January 11–February 3, 2016. Grab sampling was conducted at each of the 15 Target sampling locations during both deployment and recovery operations. Grab samples were considered supplementary and were intended for comparison purposes, but were not required for calibration purposes as they were for flume and fouling efforts (this project), and initial calibration studies (Belden et al. 2015). Grab water samples were collected in 1-L glass amber bottles by scientific divers during deployment and recovery operations. Jars were filled within a few inches of the respective POCIS sampling canister. Because of the propensity for some MC to rapidly degrade, grab water samples were extracted onsite onto Oasis HLB cartridges and frozen before shipment to the Oklahoma State University (OSU) analytical laboratory.

5.5.4. Water Quality and Current Velocity Characterization

A Troll® 9500 probe (In-Situ Inc.) was used to measure dissolved oxygen (D.O.), temperature, conductivity/salinity, and pH at multiple locations. Current velocity and direction were recorded using an Aquadopp© Profiler (Nortek AS) at the same stations. The water quality probe and current profiler were co-deployed on a weighted block system by MR divers for variable time periods (minutes to hours). Placement was on an opportunistic basis at a subset of representative stations during both the deployment and recovery efforts to obtain representative conditions during the field operations.

5.5.5. POCIS Recovery and Field Processing

POCIS canisters were deployed for 19–23 days (average 20.5 days), and upon recovery, assessed for damage and photographed. Biofouling at the Vieques site was generally very light (Figure 5-6), essentially eliminating the need to remove surficial debris or biofouling from the samplers. POCIS were individually wrapped, frozen, and shipped overnight to Dr. Jason Belden's laboratory (OSU).

Figure 5-6. Recovery and Preparation of Samplers for Shipment to Analytical Laboratory.

5.5.6. Focused Sediment and Porewater Sampling

Following the analysis of POCIS samplers, focused sediment sampling was conducted at four stations where RDX detects were above method reporting limits to assess the relative usefulness of POCIS as a screening tool for water and sediment MC contamination. The sampling design for porewater sampling is depicted in Figure 5-7. Due to the desire for low detection limits, a total of 16 60-milliliter (mL) syringes full of porewater were collected using PushPoint samplers (also known as "Henry samplers") and composited for each sample, both at representative Inner locations (~0.5 m from munition) and Outer locations (1–2 m from munition; Figure 5-7). As with grab samples collected during the POCIS demonstration, porewater was extracted onsite using Oasis HLB solid-phase extraction (SPE) cartridges under vacuum prior to freezing and shipping.

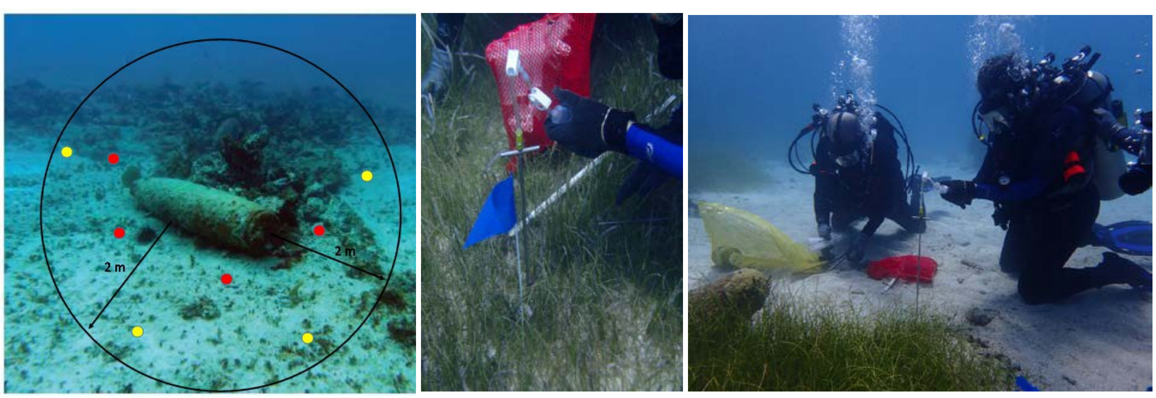


Figure 5-7. Example of Porewater Sampling ~0.5 m (red) and 1–2 m (yellow) Away from a Munition (left) and Collection of Porewater Using PushPoint Samplers (center and right).

For the sediment sampling effort, 5-inch surface sediment cores were collected—two at both the Inner and Outer sampling locations. Cores were sampled by hand by divers to ensure that placement of cores was where sediment could be obtained and in areas rendered safe from both EOD and Endangered Species Act requirements.

5.6. SAMPLING METHODS

An overview of sampling associated with the treatability studies and the demonstration at BSS is included in Section 5 of the Final Technical Report (Rosen et al. 2017). Analytical methods including instrumentation, quality assurance (QA) samples, decontamination procedures, sample documentation, and analytical data management and analysis are provided in the body and Appendix E of the Final Technical Report (Rosen et al. 2017).

For qualifying POCIS samples, the mass of MC accumulated by the POCIS were used to estimate time averaged water concentrations based on sampling rates reported in Belden et al. (2015), those refined based on current velocity (i.e., flume) experiments in this project, or those assumed—the latter being more semi-qualitative. The TWA water concentrations (C_w) were ultimately calculated using established equations provided in the Final Technical Report.

5.6.1. Compliance with Safety and Ecological Concerns

All sampling activities associated with the technology demonstration at Vieques were conducted with the knowledge and consent of relevant stakeholders, including, but not limited to, NAVFAC, NOAA, NMFS, the Puerto Rico Environmental Quality Board (PREQB), the Puerto Rico Department of Natural and Environmental Resources (PRDNER), the USACE, USEPA Region 2, and USFWS. As directed, a USACE Nationwide Permit application was filed and a letter provided by USACE indicating no permit was required as the deployment of samplers falls under activities under CERCLA at the site. Because this effort falls under CERCLA as a means to help inform and assist in the ongoing Remedial Investigation at the sites, permits were not ultimately required. Vessel strike avoidance measures (NMFS 2008) were followed to reduce the risk associated with disturbance of protected species including marine mammals such as manatees and sea turtles). Finally, experimental and dive plans for this work were vetted by NOSSA and internal Navy offices to ensure explosive safety considerations were upheld (Rosen et al. 2017).

5.7. SAMPLING RESULTS

Note: The positive control field study at Santa Rosa Sound, FL, and the technology optimization flume studies are summarized briefly in Section 2.1 and are provided in detail in the Appendices of the Final Technical Report (Rosen et al. 2017). The results shown in this section are for the technology demonstration at Vieques.

5.7.1. Recovery Success Rate

A total of 30 POCIS canisters were deployed, of which 30 (100%) were recovered. All 15 Grid canisters were in the same position they were upon deployment, verifying the performance of the sand screw-based anchoring system. Two of the Target POCIS canisters, which used the weighted block system, had slightly moved, while all others were intact. All 90 samplers (3 per canister) were intact and had relatively little fouling. Examples of deployment and recovery conditions are shown in Figure 5-5. Representative condition of the recovered samplers are provided for all items in Appendix G of the Final Technical Report (Rosen et al. 2017).

5.7.2. POCIS-Derived and Grab Sample MC Water Concentrations

Analytical results are available for 29 of the 30 (97%) samples sent to the laboratory. One sample (T5) was unavoidably compromised during sample extraction. For POCIS, TNT, 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), RDX, 4-amino-2,6-dinitrotoluene (4-ADNT), 2-amino-4,6-dinitrotoluene (2-ADNT), and 3,5-DNANIL were detected at one or more stations. For grab samples, TNT, 2,4-DNT, RDX, 4-ADNT, 2-ADNT, and 1,3,5-trinitrobenzene (TNB) were detected at one or more stations.

A summary of the detection frequency and concentration range from 14 POCIS Target samples (due to loss of one sample in the laboratory) and grab samples from the 15 Target stations for TNT and RDX is provided in Table 5-1.

Table 5-1. Detection Frequencies for POCIS and the Two Grab Time Points for TNT and RDX at Target Stations.

Sample Type Constituent		# samples	# detects	Detect frequency (%)	Concentration range (ng/L)	MDL (ng/L)	QL (ng/L)
POCIS	TNT	14	1	7	5,304	3.7	11.1
	RDX	14	11	79	5.0-12.6	2.9	8.8
Grab-Initial	TNT	15	1	7	4,470	8.4	25
	RDX	15	3	20	24-51	18	54
Grab-Final	TNT	15	1	7	7,497	8.4	25
	RDX	15	0	0	0	18	54

The largest MC detection observed in the Vieques study was at station T14, where the POCIS canister was placed approximately 12 inches away from visible breaches associated with a 1,000-lb General Purpose (GP) bomb. Divers described three half-dollar sized holes in the side of the item, which otherwise appeared intact. The average TNT concentration from the two grab samples (5,984 ng/L) was 11% higher than the POCIS sample (5,304 ng/L). The POCIS-derived average TNT concentration was 19% above the initial grab and 29% below the final grab sample concentration. Although two grab samples are unlikely to be considered representative over a three-week time period in a dynamic environment such as Roca Alcatraz, the minimal differences between the grab and TWA concentrations indicates that the breaches may have been a continuous source to the area immediately where water sampling occurred.

Although station T14 presented the highest water concentrations for nitroaromatics, RDX was not detected by either POCIS or grab samples at that station. It is interesting to note that although RDX was not detected at station T14, it was frequently detected at very low ng/L concentrations near Target and at Grid stations inside the bay. Station T14 was located south of Roca Alcatraz, outside the Bahia. In addition, many of the GP bombs were filled with Minol (mixtures of TNT, ammonium nitrate, and powdered aluminum) or Tritonol (80% TNT, 20% aluminum powder), so it is not expected that RDX would be leaking from such items.

5.7.2.1. RDX

RDX concentrations at BSS ranged from 5–13 ng/L (when detected by POCIS; Figure 5-8) and 24–51 ng/L (when detected in grab samples collected during the deployment). During the recovery grab sampling effort, all RDX grab water samples were non-detect.

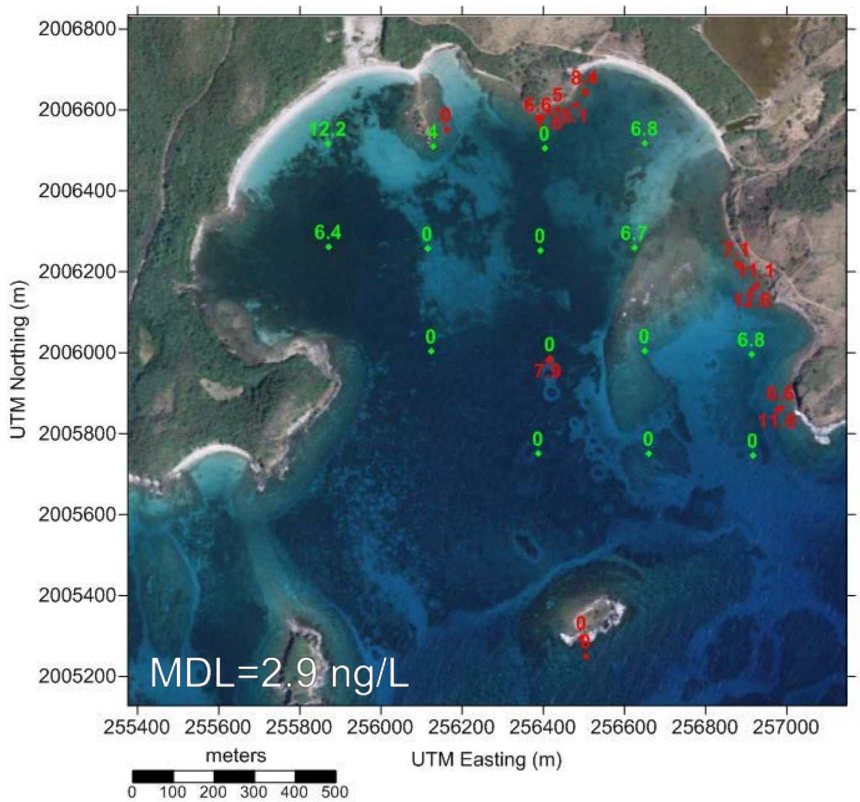


Figure 5-8. POCIS-derived TWA Concentrations Derived for RDX at 30 Stations Evaluated at BSS, Based on Method Detection Limits (MDL).

5.7.3. Detection Frequency and Magnitude at Grid Stations

The unbiased (Grid) sampling was conducted using POCIS only (i.e., water grab samples were not collected). Therefore, comparisons of Grid POCIS with grab water data cannot be made. However, comparison of the Target and Grid POCIS detection frequency and magnitude are shown in Table 5-2.

Table 5-2. Detection Frequencies of TNT and RDX for POCIS at Target and Grid.

Sample Type Constituent		# samples	# detects	Detect frequency (%)	Concentration range (ng/L)	MDL (ng/L)	QL (ng/L)
Target	TNT	14	1	7	5,304	3.7	11.1
	RDX	14	11	79	5.0-12.6	2.9	8.8
Grid	TNT	15	1	7	9.6	3.7	11.1
	RDX	15	6	40	4.0-12.2	18	54

5.7.3.1. TNT

Only one TNT detect was observed for each of the Target and Grid sampling approaches. The Grid detect was three orders of magnitude lower than that quantified from the Target breached munition. The Grid value was above the MDL, but slightly below the QL. The marginal detect occurred at station D3, which is in relatively close proximity to the *ex-USS KILLEN* (a US Navy target ship; Deslarzes et al. 2002). The detect at station T14 was within 6–12 inches of a 1,000-lb GP bomb with visible breaches at the placement location.

5.7.3.2. RDX

Detection frequency was nearly twice as high for Target stations in comparison to Grid stations (79% and 40%, respectively). The concentrations were very similar, averaging 8.1 and 7.2 ng/L, respectively. Combined, 4 of the total 17 detects were above the QL. In general, RDX detects, including at Grid stations, were more often closer to the shoreline as opposed to the center of the bay, where most samples were below detection limits.

5.7.4. Site-Specific Current Velocities and POCIS Sampling Rates

The Nortek current profiler results from opportunistic sampling during POCIS deployment and recovery efforts are provided in the Final Technical Report (Rosen et al. 2017) and were used to develop site-specific sampling rates based on current velocity curves fitted from the flume studies summarized in the Appendices of the Final Technical Report.

5.7.5. Porewater and Sediment Sampling Results

All porewater and sediment concentrations were below method detection limits (MDLs), 3–18 ng/liter (L) and 0.5–3.4 micrograms (µg)/kilogram (kg) dry weight, respectively. The lack of detected MC concentrations in porewater and sediment demonstrate that the water column was the most conservative compartment for detecting MC in this study. Sediment organic carbon and grain size distributions for the focused sediment and porewater sampling study are provided in the Final Technical Report (Rosen et al. 2017).

5.7.6. Quality Assurance and Quality Control (QA/QC)

All blanks, including grab water, porewater, POCIS, and sediment were below QLs (8–54 ng/L, 8–54 ng/L, and 0.5–3.4 µg/kg dry weight, respectively; see Rosen et al. 2017). Extraction recoveries for laboratory and matrix spikes were acceptable for all matrices. Efficiencies for field spiked grab samples, laboratory spiked water, and laboratory spiked sediment ranged from 84–95%, 81–107%, and 73–101%, respectively. Extraction efficiencies from POCIS (spiked HLB adsorbant) ranged from 95–120% and Relative Standard Deviations were <10% for each analyte. All sampling holding and instrument quality control (QC) criteria were met. Water samples were extracted in the field to obtain <48-hour holding time.

5.7.7. Comparison of Field Data with Toxicity Screening Values

Lotufo et al. (2017) calculated hazardous concentration values for 5% of species (HC5), or protective at the 95% confidence interval, for 13 common conventional MC based on effects and no-effects concentration data from the literature, inclusive of the most recent toxicity data available.

Concentrations for MC at BSS were generally 4–6 orders of magnitude (10,000–1,000,000 times) lower than the HC5 (Table 5-3). The single TNT value over the QL was 1 order of magnitude (10 times) and 2 orders of magnitude (100 times) lower than no-effects and effects-based HC5 values, respectively. For comparison, the highest concentrations for TNT (0.103 µg/L) and RDX (0.097 µg/L) reported outside the source canister in the positive control experiment at Santa Rosa Sound, FL (Rosen et al. 2017) were 4 and 6 orders of magnitude lower than effects based HC5 values, respectively, similar to those observed at BSS.

Table 5-3. Comparison of Concentrations Observed at BSS and HC5 Concentrations for Both Effects and No-effects-based Toxicity.

MC	Concentration Range at Site (µg/L)	HC_5 (µg/L)		# orders of magnitude below HC_5	
		Effects	No effects	Effects	No effects
2,4,6-TNT	0.0096-5.3	116	34	2-6	1-5
2-ADNT	0.054	1,239	NA	6	NA
4-ADNT	0.103	1,983	NA	5	NA
1,3-DNB	0.009	274	39	6	5
2,4-DNT	0.046	615	43	5	4
RDX	0.004-0.013	2,074	4,560	5-6	4-5

2,4,6-TNT: 2,4,6-trinitrotoluene

HC5: Hazardous concentration for 5% of species (from Lotufo et al. 2017)
NA: <6 species. No calculation available.

Page Intentionally Left Blank

6. PERFORMANCE ASSESSMENT

6.1. QUANTITATIVE PERFORMANCE OBJECTIVES

6.1.1. Performance Objective #1: Detection of MC in Controlled Field Study

Performance Objective 1 was the verification that POCIS could detect MCs in a positive control field study at a clean site. Following permit approvals, 15 grams of Comp B (an explosive fill composed of 39.5% TNT, 59.5% RDX, 1% wax) was placed at the site over a 13-day exposure. The performance objective was met, with POCIS-derived TNT and RDX average water concentrations ranging from 9–103 ng/L, with the highest concentrations within 0.3 m of the source. MC was non-detectable at stations >2 m from the source. Grab water samples collected and oyster tissues deployed at the site were below detection limits for all stations, indicating POCIS was the most sensitive technology for ultra-trace level detection in a controlled field study.

6.1.2. Performance Objective #2: Accurate Quantification of TWA MC Concentrations

Performance Objective 2 was the verification that POCIS-derived TWA water concentrations and TWA concentrations derived from multiple grab sampling would produce similar results, or better results for POCIS in a flume study simulating field conditions or in actual field studies. This objective was met for the Comp B flume study, the positive control field study, and the Vieques field validation study. Comp B flume-deployed POCIS estimated TWA water concentrations for TNT and RDX that were similar to averaged concentrations generated using multiple grab TWA concentrations. In the positive control field study, MC concentration was successfully determined using POCIS, while the discrete-sampling-derived concentrations as grab water samples resulted only in non-detects. In the Vieques field validation study, 1 of 30 sampling locations resulted in a relatively high water column concentration for TNT and several of its transformation products. The average TNT concentration from the two grab samples at the station was only 11% higher than the POCIS sample. The POCIS-derived average TNT concentration was 19% above the initial grab and 29% below the final grab sample concentration. POCIS-derived average RDX concentrations for 11 stations had detectable concentrations, while at the same locations only 3 stations had detectable concentration from grab samples during the initial period, and all stations were non-detect for the final period. Overall, data from grab samples validated the data obtained using POCIS for all the flume and field studies.

6.1.3. Performance Objective #3: Accurate Quantification Under Different Flow Velocities and Encapsulation Conditions

Performance Objective 3 was the demonstration of the effects of varying current velocities in a series of controlled flume studies with precise velocity control on the uptake of MC from spiked water to optimize sampling rates based on site-specific flow velocities. The objective was met, with a positive, statistically significant, linear relationship between current velocity and sampling rate for POCIS for multiple MC, providing useful means of applying appropriate sampling rates. From the regression equations derived, simple calculations are able to be used to correct for flow velocity if such measurements are made at the field site. In this project, a Nortek current profiler was used at Vieques to calculate the most accurate sampling rate based on measured flow.

Two different explosive fill encapsulation scenarios showed highly comparable TWA concentrations for POCIS and average from multiple grab samples.

6.1.4. Performance Objective #4: Detection of MC at Levels Substantially Lower Than Achievable for Water Samples

Performance Objective 4 was the demonstration that POCIS would detect MC at levels substantially lower than achievable using typical grab sampling methods. The performance objective was met. The QL for POCIS- derived TWA concentrations were consistently lower than those derived for discrete samples. Lower detection limits are achieved using POCIS sampling because the estimated volumes of water cleared of MC during the deployment time were substantially greater than the volume (1 L) consistently of all grab water samples. For the Comp B positive control study, the concentrations of TNT and RDX in grab samples were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 12 out of 20 stations. For 12 stations out of 15 in the Vieques field validation study, the concentrations of RDX in grab samples were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 8 out those 12 stations.

6.1.5. Performance Objective #5: Success Rate

Performance Objective 5 was the demonstration of the success rate in terms of both recovery of POCIS from the field and the determination of useful data. The performance objective was met. A total of 20, 51, and 30 POCIS canisters (each containing 3 samplers) were deployed in the positive control field study, in the flume studies, and at the Vieques site. All samplers (100%) were recovered. Data were considered useful whether or not the concentrations were above or below MDLs, as it was expected that many field samples would be non-detect. All flume study data resulted in measurable concentrations, as the flume was spiked at concentrations to ensure detects. The strong correspondence between POCIS and multiple grab-based TWA concentrations in flume studies (Rosen et al. 2017) are a quantitative measure of the value of the POCIS data, showing negligible losses and post-uptake preservation of the parent compounds throughout the exposures.

6.1.6. Performance Objective #6: QC and QA

Performance Objective 6 was the demonstration that all field and laboratory efforts followed experiment-specific QA objectives and that QC criteria were met. All criteria were mostly met for this part of the project. Blanks, including field and laboratory, did not have MCs above the QLs. All spike tests had accuracy and relative precision within 25% of expected. In addition, all other sampling handling and instrument criteria were also met. A few analytes in tissue and sediment had recoveries up to 30% lower. See Appendix E of the Final Technical Report (Rosen et al. 2017) for more details.

6.2. QUALITATIVE PERFORMANCE OBJECTIVES

6.2.1. Performance Objective #7: Successful Assessment of Potential MC Exposure at UWMM Site

Performance Objective 7 was the demonstration of the ability to use POCIS TWA data for MC to evaluate ecological risk based on comparison with toxicity benchmarks developed from species sensitivity distributions. Instead of largely non-detects from grab samples, POCIS reported ≥ low ng/L MC concentrations in all tasks, allowing more quantitative assessment, but negligible ecological risk based on comparison with species sensitivity distributions. For Vieques, POCIS- derived TWA concentrations were 10–1,000,000 times lower than HC5 generated from the most up-to-date and comprehensive species sensitivity distributions (SSD) as reported by Lotufo et al. (2017). Despite POCIS having a higher frequency of detection than grab samples at Vieques, the grab samples and POCIS were shown to be of equal value for CERCLA risk assessment because the detection levels for grab sampling were below regulatory screening levels. Therefore, both sampling methods clearly showed no unacceptable risk. The performance objective was met.

6.2.2. Performance Objective #8: Ease of Operator Use

Performance Objective 8 was a qualitative objective of ease of operator use, requiring feedback from field and laboratory technicians on the usability of technology, sample preparation and extraction, and time requirements. This performance objective was met. At Vieques, feedback in the field from Navy and contractor personnel was mixed. The deployment and recovery of POCIS went well, but the overall process was highly labor-intensive, with dive teams and boat support required for both deployment and recovery of the samplers. The use of divers creates significant safety concerns associated with POCIS. Overall, the level of effort and the associated safety concerns for POCIS are much higher than grab sampling, which can be done in a single field effort without divers. Site managers understood the benefits of integrative sampling and the potential advantages of providing enhanced credibility through lower detection limits and obtaining data representative over extended timeframes, thereby sampling over a larger area. Grab sampling representative of an integrative sampler would require substantially more labor but depends on site-specific logistics and study objectives. Similarly, autosampling would require multiple trips to the site to obtain an integrated sample over time and ensure that MC do not degrade (e.g., freeze or extract samples daily). Laboratory feedback indicated that processing of POCIS in comparison with standard SPE of grab water samples was negligible.

6.2.3. Performance Objective #9: Cost-Benefit

Performance Objective 9 was the demonstration that the relative value of data from POCIS compared well with the cost of measurements from water and sediment porewater. This performance objective was met. POCIS was the only technology that detected MC at Gulf Breeze, and had a higher frequency of detects compared to grab sampling at Vieques. The costs of using POCIS over more traditional means of water sampling (e.g., grab or composite sampling) are examined using multiple examples in the Cost Analysis (Section 7.0) and suggest that POCIS are less expensive when traditional sampling involves multiple sampling events to develop an integrative sample (as opposed to single grab samples that would be less expensive than POCIS).

However, for sites where regulatory requirements are for single grab samples, the costs for a POCIS-based program can be considerably higher. Vieques is a complex site and the demonstration was designed to maximize likelihood for detecting a leaking munition. It is unlikely that POCIS would be routinely applied in such a manner in a monitoring or regulatory program.

6.2.4. Performance Objective #10: End-User Understanding and Acceptance

Performance Objective 10 was the qualitative objective of end-user understanding and acceptance of the POCIS technology for potential use at UWMM sites. This performance objective was met. Site managers and contractors understood the value of integrative samplers for MC, and provided a considerable amount of in-kind support to successfully demonstrate the technology at Vieques. The notion that POCIS would help with the criticisms of sampling at the wrong time and at the wrong place was seen as a primary advantage for the Gulf Breeze study. Site managers at Vieques expressed concerns about the cost, diver safety, and difficulty of implementing POCIS. Site managers also noted that the grab samples matched well with the POCIS results and the grab samplers are accepted by the regulators for risk assessment at the site. Although the cost for POCIS is less than grab or composite sampling based on a sampling program that would produce similarly integrative samples (see Section 7.0), the cost of collecting a single grab sample at a site would be less expensive than monitoring with POCIS. The cost of POCIS at UWMM sites will be site-specific and dependent of study objectives. Cost scenarios to develop integrative samples with POCIS in comparison to other means are described in Section 7.0.

7. COST ASSESSMENT

7.1. COST MODEL

7.1.1. Cost Model for Demonstration of POCIS at a DoD UWMM Site

The demonstration at BSS involved placement of 30 POCIS canisters for 3 weeks. The costs associated with the demonstration involved a reconnaissance survey to identify candidate munitions for demonstrating the technology, an anchoring trial, deployment and recovery phases, a focused sediment sampling validation effort, and comparisons of water concentrations measured from the field site with screening benchmarks for toxicity. Note that the costs of conducting this study at BSS are heavily influenced by the logistical challenges associated with accessing the site with MR and scientific divers. POCIS and grab sampling of water for MC analysis includes placement and monitoring costs for the demonstration project. Field work costs do not include management, oversight, and coordination.

Uncertainties associated with costing for POCIS application depend substantially on safety requirements on a site-specific basis. Total cost for the Vieques Demonstration at BSS was calculated as $369,300, as detailed in the Final Technical Report, Section 7 (Rosen et al. 2017).

7.1.2. Cost Model for Implementation of POCIS at Underwater UWMM Sites

Implementation of the POCIS technology as a monitoring tool at UWMM sites unrelated to this demonstration project would likely require fewer site visits and less rigorous monitoring, due to the comprehensive nature of the demonstration at Vieques (e.g., target and unbiased sites, sediment sampling, reconnaissance survey). For implementation, it is assumed that an unbiased approach to deployment would more likely be required by a regulator. This assumes that historical knowledge of where UWMM are located are available. A cost model for implementation of POCIS at other UWMM sites, assuming similar requirements (e.g., MR and scientific divers) is detailed in Section 7 of the Final Technical Report (Rosen et al. 2017). The cost model assumes a site visit, deployment and recovery at 15 monitoring locations, chemical analysis, and reporting, and is estimated to cost $155,400.

7.2. COST DRIVERS

Cost drivers to consider in selecting this technology include:

- ***Monitoring or regulatory requirements:*** The POCIS technology provides a measure of polar/weakly hydrophobic contaminants such as MC by integrating over time and sampling relatively large volumes of water in comparison with grab samples that quantify one point in time for a given sampling event. As stated above, if a regulatory program seeks the most conservative exposure possible from a breached munition, identification of that breached munition can become extremely costly, as it involves the considerations of searching for a ‘needle in a haystack.’ If the program is satisfied with monitoring for MC using a non-biased grid-style approach as demonstrated, costs and logistical constraints become much simpler, and arguably just as ecologically relevant, and still include the advantages of the integrative nature of POCIS over grab sampling.

- ***Safety considerations and diver requirements:*** Approximately 25% of the budget associated with monitoring a UWMM site using POCIS is expected to be associated with dive and safety plans, permitting, and travel and labor associated with specialized dive teams certified for sampling at sites where UXO are present. At Vieques, three MR divers and two scientific divers were required to execute the demonstration.
- ***Comparative sampling:*** The integrative nature of POCIS (i.e., 2–3 weeks of continuous sampling) contrasts with grab samples that capture one point in time. Therefore, autosamplers, such as *in situ* chemical oxidation (ISCO) samplers commonly used to collect representative samples for stormwater monitoring and compliance, are a more logical comparison with POCIS than grab sampling. However, because nitroaromatics degrade rapidly and need to be extracted as soon as practical, autosampler bottles would have to be changed daily to preserve sample integrity, requiring more site visits. Further, ISCO samplers typically require regular maintenance while the POCIS is maintenance-free. Finally, costs can vary significantly based on site complexity including considerations for bathymetry, currents, infrastructure, and access.

7.3. COST ANALYSIS

To evaluate and compare the costs of integrative water sampling using POCIS with alternative approaches (e.g., composite or grab sampling), three scenarios were considered. The scenarios include (1) a shallow bay where 15 stations are monitored using a diver-installed mooring for attachment of POCIS; (2) a lagoon where POCIS are deployed around the perimeter at 6 monitoring stations, also requiring divers; and (3) a scenario similar to the positive control study at Gulf Breeze where physical structures are available to suspend 15 POCIS canisters, eliminating the requirement for divers. Costs are driven by labor, equipment, laboratory analysis, supplies, and transportation costs.

7.3.1. Site 1

Site 1 represents a 100-acre bay in shallow water adjacent to a former DoD training range. The bay has already undergone a series of surveys to locate munitions, and items of relatively unknown condition are widely present throughout the bay. The approach involves an unbiased (i.e., Grid) design incorporating 15 stations approximately equidistant from one another for a two-week exposure. The costs associated with POCIS monitoring at Site 1 are $155,540 (see Section 7 of Final Technical Report [Rosen et al. 2017]). The design involves full MR and scientific dive teams on both the deployment and recovery phases, requiring two trips to the site for deployment and recovery phases.

7.3.1.1. Grab Sampling

As discussed previously, grab sampling and integrative sampling with passive samplers are inherently different. A minimum of two grab samples per station per day—one during an incoming tide and one during an outgoing tide—over the 14-day period was deemed required to develop a composite sample representative of an 'integrated' sample but is still not equivalent to continuous sampling. Due to the relatively shallow nature of the site, it is assumed that the samples could be collected using a simple pole sampler or peristaltic pump from a boat without diver support but assumes that one EOD technician would be required to be onsite.

The sampling still requires two boats—a sampling boat and a support boat—and would require 14 consecutive days of travel to and from the site for a small project team. The costs of this scenario equates to $239,740, a 54% increase over POCIS deployments with a full dive crew.

7.3.1.2. Composite Sampling

Composite sampling with autosamplers is not a viable option at this site due to the lack of placement locations for the sampling systems over open water.

7.3.2. Site 2

Site 2 represents a 20-acre lagoon, potentially impacted by a training range with numerous munitions known to be present. The study design involves a 2-week POCIS deployment within approximately 50 feet of the shoreline around the lagoon perimeter at a total of 6 monitoring (non-biased) stations. This scenario also requires MR and scientific divers during deployment and recovery phases, but it is anticipated that all stations would be serviced in one field day for each deployment and recovery phase. The costs for a POCIS program at this site are estimated at $111,125 and are detailed in Section 7 of the Final Technical Report (Rosen et al. 2017).

7.3.2.1. Grab Sampling

Grab sampling at Site 2 would not require MR or scientific divers, but it is assumed that a single EOD technician would be required during sampling. Sampling would be collected at each of the six non-biased monitoring stations with a pole sampler or peristaltic pump from the sampling boat. It is anticipated that one boat would be required for this sampling effort. However, to be comparable with an integrated sample generated by POCIS, multiple grab samples would have to be collected, archived, and later composited to produce integrated (e.g., composite) samples. Under this regime, it is assumed that a single sample per day would be sufficient, as the lagoon is not tidally influenced and is characterized by low-flow velocities. This still requires 14 trips to the site, at a total cost of $207,740, or 87% greater than POCIS sampling.

7.3.2.2. Composite Sampling

Due to the proximity to the shoreline, composite sampling using ISCO autosamplers would be an option. It is assumed that the autosamplers would be rented for a 3-week period for a 2-week deployment at the 6 stations around the lagoon, approximately 50 feet from the shoreline as projected for the POCIS deployment. This approach would require MR and scientific divers during two time points only—one day at the beginning of the study to place sampling tubing securely at the targeted locations and then during the final day to ensure all underwater equipment was appropriately recovered. The composite sampling would require daily visits to the site by a terrestrial-based technical field team of two people to recover and process a daily sample (samples need to be extracted and/or frozen within 24 hours of collection to prevent transformation of MC), install new sample bottles, re-program samplers, and troubleshoot the autosamplers as necessary. Because the majority of the field team will be onsite during the entire process, costs are primarily weighted towards the “Deployment and Maintenance” cost element. The cost of this effort is estimated at $178,875, or 61% greater than POCIS sampling.

7.3.3. Site 3

Site 3 is a bay where DMM are of potential concern. This is in a highly industrialized area where munitions were discarded over a 3-acre area adjacent to a Navy base where multiple structures (i.e., piers, docks, etc.) are available for suspending POCIS within sufficient proximity to sources based on historical knowledge of where the DMM are present. This site does not require usual safety disclosures or diver support typical of an underwater MR site, as all work would be conducted out of the water and no equipment would come into contact with the munitions. This scenario is somewhat analogous to the positive control study conducted at Gulf Breeze (see Appendix B of Final Technical Report) where samplers would be placed in the vicinity of known or suspected breached items or where large clusters of munitions are known to occur. The site is characterized as a depth of approximately 40 feet during the average low tide during the sampling study; therefore, POCIS canisters would be tied off on appropriate floating structures that would allow continuous exposure approximately 3–5 feet above the sediment bed. A total of ten POCIS canisters would be deployed at this site at ten stations. The costs for a POCIS program at this site are estimated at $102,735 and are shown in detail in Section 7 of the Final Technical Report (Rosen et al. 2017).

7.3.3.1. Grab Sampling

As discussed previously, grab sampling and integrative sampling with passive samplers are inherently different. A minimum of two grab samples per station per day—one during an incoming tide and one during an outgoing tide—over the 14-day period would be required to develop a composited sample somewhat representative of an ‘integrated’ sample involving continuous passive sampling. Based on the target sampling at a depth of 35 feet below a floating structure, it is assumed that Niskin bottles will be used to collect grab samples approximately 3–5 feet above the sediment bed. This scenario would not require MR divers or boat support but would require 14 consecutive days of sampling twice a day for a two-person technical team. The costs of this scenario equate to $126,735, a 23% increase over POCIS deployments.

7.3.3.2. Composite Sampling

Due to access to a series of floating docks at the site, composite sampling using ISCO autosamplers would be an option. It is assumed that the autosamplers would be rented for a 3-week period for a 2-week deployment at the 10 stations. The approach does not involve divers, as autosamplers would be installed on the docks and peristaltic pumps would be used to collect the samples from a designated depth (e.g., 3–5 feet above sediment bed). The composite sampling would require daily visits to the site by a terrestrial-based technical field team of two people to recover and process a daily sample (samples need to be extracted and/or frozen within 24 hours of collection to prevent transformation of MC), install new sample bottles, re-program samplers, and troubleshoot the autosamplers as necessary. Because most of the field team will be onsite during the entire process, costs are primarily weighted towards the “Deployment and Maintenance” cost element. The cost of this scenario equates to $164,735, a 60% increase over POCIS deployments (see Section 7.0 of the Final Technical Report [Rosen et al. 2017] for details).

8. IMPLEMENTATION ISSUES

The advantages of POCIS have been increasingly demonstrated over the past 10–15 years since early publications demonstrating their utility for monitoring polar and weakly hydrophobic organics (e.g., Alvarez et al. 2004, Harman et al. 2012, Morin et al. 2012). The continuous sampling approach allows TWA concentrations, and the detection of chemicals that rapidly dissipate or degrade in the environment following release from the source (Alvarez et al. 2004, Mazzella et al. 2008). Unlike samplers that rapidly achieve equilibrium using very high surface-area-to-sorbent volume, POCIS exhibits negligible loss rates and does not require long times to reach equilibrium, allowing small masses of chemical from episodic release events to be retained in the device by the end of the deployment period. The POCIS vastly simplifies sampling and preparation steps by elimination of electrical or fuel powering requirements, significantly reduces the numbers of analyses required, and provides protection of analytes against decomposition during transport and storage (Kot-Wasik et al. 2007). POCIS data can subsequently be used to assess ecological risk due to MC exposure based on propensity for uptake and toxicity to biota without having to make such measurements (Alvarez et al. 2012).

Previous laboratory proof of concept work for MC by this project team (e.g., Belden et al. 2015), and the demonstration and validation of POCIS in laboratory and field efforts for this project indicate the technology is highly valuable for assessment of MC exposure at UWMM sites. POCIS-derived TWA concentrations are expected to be more informative about exposure to MC compared to discrete grab samples when MC concentrations are low and MC is released to the water column in a time-varying nature, either from UWMM (Wang et al. 2013) or from terrestrial-based time varying inputs (e.g., runoff events or tidal pumping of groundwater contaminated with MC). For most applications, the cost associated with POCIS sampling is less than that for multiple grab or composite sampling required to represent a comparably integrated sample (see Section 7). In addition, POCIS sampling is expected to directly address sentiment from those concerned with UWMM as sources of contamination and who perceive grab sampling may take place at the wrong time, in the wrong place, and with insufficient detection limits, and therefore fail to adequately characterize exposure risk potential. UWMM site characterization using POCIS addresses all three of these concerns, and implementation as part of monitoring programs or for risk assessment should be considered depending on the site-specific objectives. Site characterization using POCIS may be site-wide or spatially focused or may be used to complement traditional sampling approaches to identify or rank sites of potential concern and support LIP versus removal decision-making processes.

One of the unique aspects of this project involved the optimization of POCIS sampling rate for variable flow velocities based on a series of large scale flume studies where flow velocity was precisely controlled. That study was designed to improve the semi-quantitative nature of POCIS in comparison with more traditional water sampling. The contaminant-specific R_s, used for estimation of a TWA water concentration by POCIS, is dependent on a variety of *in situ* exposure conditions including flow, salinity, pH, temperature, dissolved organic compounds, and biofouling. That said, most of these variables appear to have overall minimal effect on R_s (Harman et al. 2012). Efforts to improve the quantitative ability of POCIS are ongoing, including a recently completed SEED project (SERDP 2016) that found promise using nylon mesh to reduce flow effects and/or to incorporate micro-flow sensors into the exposure canister for precise *in situ* flow measurements for optimal R_s determination.

Page Intentionally Left Blank

9. REFERENCES

Alvarez DA, Petty JD, Huckins JN, Jones-Lepp TL, Getting DT, Goddard JP, Manahan SE. 2004. Development of a passive, *in situ*, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environmental Toxicology and Chemistry 23: 1640-1648.

Alvarez DA, Rosen MR, Perkins SD, Cranor WL, Schroeder VL, Jones-Lepp TL. 2012. Bottom sediment as a source of organic contaminants in Lake Mead, Nevada, USA. Chemosphere 88:605–611.

ATSDR (Agency for Toxic Substances and Disease Registry). 2006. Agency for Toxic Substances and Disease Registry, 2006. Health consultation: Land crab evaluation. National Oceanic and Atmospheric Administration Data. Isla de Vieques. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Division of Health Assessment and Consultation. 22 pp.

Bauer LJ and Kendall MS (eds.). 2010. An Ecological Characterization of the Marine Resources of Vieques, Puerto Rico Part II: Field Studies of Habitats, Nutrients, Contaminants, Fish, and Benthic Communities. NOAA Technical Memorandum NOS NCCOS 110. Silver Spring, MD. 174 pp.

Belden JB, Lotufo GR, Biedenbach JM, Sieve KK, Rosen G. 2015. Application of POCIS for exposure assessment of munitions constituents during constant and fluctuating exposure. Environ. Toxicol. Chem. Doi: 10.1002/etc.2836.

Bueno, M.J.M., Herrera, S., Munaron, D., Boillot, C., Fenet, H., Chiron, S., Gomez, E., 2016. POCIS passive samplers as a monitoring tool for pharmaceutical residues and their transformation products in marine environment. Environ. Sci. Pollut. Res. 23, 5019-5029.

Capella JE, Alston DA, Cabarcas-Nύñez A, Quintero-Fonseca H, Cortés R. 2003. Oceanographic Considerations for offshore Aquaculture on the Puerto Rico-U.S. Virgin Island Platform. pp. 247-261. In: CJ Bridger and BA Costa-Pierce, editors. Open Ocean Aquaculture: From Research to Commercial Reality. The World Aquaculture Society Baton Rouge, LA, USA.

CH2M HILL. 2007. East Vieques background soil inorganics investigation report: former Vieques Naval Training Range, Vieques, Puerto Rico. Prepared for the Department of the Navy, Atlantic. Contract No. N62470-02-D-3052-CTO-039. 212 pp.

CH2M HILL. 2013. Draft Final Site Management Plan Fiscal Year 2014. Atlantic Fleet Weapons Training Area – Vieques. Vieques, Puerto Rico. Prepared for Naval Facilities Engineering Command, Department of the Navy Atlantic, Contract No. N62470-08-D-1000, CTO-037, September 2013. 96 pp.

Deslarzes K, Nawojchik R, Evans D. 2002. Ex-USS Killen Site Investigation and Biological Characterization, Vieques Island, Naval Station Roosevelt Roads, Puerto Rico. Final Report Contract No. N62470-95-D-1160, Naval Facilities Engineering Command, Atlantic Division, Geo-Marine, Inc., June 2002.

GMI (Geo-Marine, Inc.). 2003. Reef ecosystem baseline assessment survey and monitoring, Vieques Island, Naval Station Roosevelt Roads, Puerto Rico. Prepared for Atlantic Division, Naval Facilities Engineering Command, Norfolk, Virginia.

GMI. 2007. Preliminary underwater survey of muntions related items and non- munitions debris, Vieques Island, Puerto Rico. Final report – July 2007. Prepared by GMI Marine Sciences Group, Plano, TX, for Naval Facilities Engineering Command. Contract No. CH2M HILL #918383 Vieques. 70 pp.

Harman C, Allan IJ, Vermeirssen ELM. 2012. Calibration and use of the polar organic chemical integrative sampler- A critical review. Environ. Toxicol. Chem. 2012, 31, 2724– 2738

Kot-Wasik A, Zabiegala B, Urbanowicz M, Dominiak E, Wasik A, Namiesnik J. 2007. Advances in passive sampling in environmental studies. Analytica Chimica Acta 602: 141-163.

Lewis J, Martel R, Trepanier L, Ampleman G, Thiboutot S. 2009. Quantifying the transport of energetic materials in unsaturated sediments from cracked unexploded ordnance. Journal of Environmental Quality 38: 2229-2236.

Li H, Vermeirssen LM, Helms PA, Metcalfe CD. 2010. Controlled field evaluation of water flow rate effects on sampling polar organic compounds using Polar Organic Chemical Integrative Samplers. Environmental Toxicology and Chemistry. 29:2461-2469.

Lotufo GR, George RD, Belden JB, Woodley CM, Smith DL, Rosen G. 2018. Field validation of an integrative passive sampler for use at underwater munitions sites. Investigation of polar organic chemical integrative sampler (POCIS) flow rate dependence for munitions constituents in underwater environments. Environ. Monit. Assess. 190:171.

Lotufo GR, Lydy MJ, Rorrer GL, Cruz-Uribe O, Cheney DP. 2009. Bioconcentration, Bioaccumulation and Biotransformation of Explosives and Related Compounds in Aquatic Organisms. In Sunahara, G.I., Lotufo, G.R., Kuperman, R.G., Hawari, J., eds, Ecotoxicology of Explosives. CRC, Boca Raton, FL.

Lotufo GR, Chappell MA, George RD, Ballentine ML Price CL, Glisch EJ, Fuentes AA, Bridges TS. 2017. Review and Synthesis of Evidence Regarding Environmental Risks Posed by Munitions Constituents (MC) in Aquatic Systems. Final report to SERDP for project ER-2341. ERDC/EL TR-17-X. US Army Engineer Research and Development Center, Vicksburg.

Lotufo GR, Rosen G, Wild W, Carton G. 2013. Summary Review of the Aquatic Toxicology of Munitions Constituents. US Army Corps of Engineers Engineer Research and Development Center (ERDC), Technical Report ERDC/EL TR-13-8. June 2013. 124 pp.

Mazzella N, Debenest T, Delmas F. 2008. Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment. Chemosphere 73: 545-550.

McDonald J. 2009. UXO Detection and Characterization in the Marine Environment. Travelogue and Phenomenology Report, ESTCP Project MM-0324, July 2009. 60 pp.

Miege C, Budzinski H, Jacquet R, Soulie, C, Pelte T, Coquery M. 2012. Polar organic chemical integrative sampler (POCIS): application for monitoring organic micropollutants in wastewater effluent and surface water. J Environ Monit. 14:626-635.

Morin N, Mie`ge C, Random J, Coquery M. 2012. Chemical calibration, performance, validation and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments. TrAC Trends in Analytical Chemistry 36:144-175.

Munaron D, Tapie N, Budzinski H, Andral B, Gonzalez J-L. 2012. Pharmaceuticals, alkylphenols and pesticides in Mediterranean coastal waters: Results from a pilot survey using passive samplers. Estuarine, Coastal and Shelf Science 114: 82-92.

NAVFAC. 2011. Second Five-Year Review: Jackson Park Housing Complex/Naval Hospital Bremerton. Naval Facilities Engineering Command Northwest. Final Report. 4 January 11.

NMFS (National Marine Fisheries Service). 2008. Southeast Region Vessel Strike Avoidance Measures and Reporting for Mariners; http://sero.nmfs.noaa.gov/protected_resources/section_7/guidance_docs/documents/copy_of_ vessel_strike_avoidance_february_2008.pdf. Revised February 2008.

NOAA and Ridolfi. 2006. Final data report for the Vieques Island biota sampling project, Vieques Island, Puerto Rico. National Oceanic and Atmospheric Administration (NOAA) Office of Response and Restoration and RIDOLFI Inc. Seattle, WA.

Pait AS, Mason AL, Whitall DR, Christensen JD, Hartwell SI. 2010. Assessment of Chemcial Contaminants in Sediments and Corals in Vieques. In: Bauer and Kendall (eds.), An Ecological Characterization of the Marine Resources of Vieques, Puerto Rico Part II: Field Studies of Habitats, Nutrients, Contaminants, Fish, and Benthic Communities. NOAA Technical Memorandum NOS NCCOS 110. Silver Spring, MD. 174 pp.

Pascoe GA, Kroeger K, Leisle D, Feldpausch RJ. 2010. Munition constituents: Preliminary sediment screening criteria for the protection of marine benthic invertebrates. *Chemosphere* 81:807-816.

Porter JW, Barton JV, Torres C. 2011. Ecological, radiological, and toxicological effects of naval bombardment on the coral reefs of Isla de Vieques, Puerto Rico. pp 65-122. In *Warfare Ecology*. Netherlands: Springer.

Rosen G, Lotufo GR, George RD, Wild W, Rabalais L, Morrison S, Belden JB, 2018. Field validation of POCIS for monitoring munitions constituents at underwater military munitions sites. Environ. Toxicol.Chem. 37:2257-2267.

Rosen G, George R, Wild W, Colvin M, Guerrero J, Lotufo G, Woodley C, Smith D, Belden JB. 2017. Validation of Passive Sampling Devices for Monitoring of Munitions Constituents in Underwater Environments. Final Technical Report to the Department of Defense Environmental Security Technology Certification Program. SPAWAR Technical Report #3076.https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-201433/ER-201433.

Rosen G, Lotufo GR. 2010. Fate and effects of Composition B in multi-species marine exposures. Environ. Toxicol. Chem.29:1330-1337.

SERDP (Strategic Environmental Research and Development Program). 2010. White Paper, Munitions in the Underwater Environment: State of the Science and Knowledge Gaps. June. 12pp.

SERDP. 2016. Optimization of Integrative Passive Sampling Approaches for Use in the Epibenthic Environment, Final Report. #ER-2542.

SERDP. 2017. Review and Synthesis of Evidence Regarding Environmental Risks Posed by Munitions Constituents (MC) in Aquatic Systems, Final Report. #ER-2341.

United States Army Corps of Engineers (USACE). 2013. Former Seattle naval supply depot piers 90 and 91- Port of Seattle, WA.: Formerly used defense site #F10WA012501, remedial investigation/Final report. Contract No. W9128F-10-D-0058, Delivery Order 04. Omaha, NE: U.S. Army Corps of Engineers, Omaha District.

University of Hawaii (UH). 2014a. Final environmental study: Ordnance Reef (HI-06), Wai'anae, O'ahu, Hawai'i. Contract No. N00024-08-D-6323. Prepared for the U.S. Army Corps of Engineers.

University of Hawaii (UH). 2014b. Ordnance Reef (HI-06) follow-pp investigation, final assessment report. NDCEE-CR-2013-170. Contract No. W91ZLK-10-D-005, Task 0773. Johnstown, PA: National Defense Center for Entergy and Environment.

Wang PF, George RD, Wild WJ, Liao Q. 2013. Defining munition constituent (MC) source terms in aquatic environments on DoD ranges (ER-1453). Final report. Space and Naval Warfare Systems Center (SPAWAR) Technical Report #1999. January 2013. 130 pp. https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Identifying-and-Evaluating-Sources/ER-1453/ER-1453/(language)/eng-US.

Page Intentionally Left Blank

APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Fax E-mail	Role in Project
Mr. Gunther Rosen	SSC Pacific 53475 Strothe Rd. San Diego, CA 92152	Tel: (619) 553-0886 Fax: (619) 553-6305 rosen@spawar.navy.mil	PI, Project management, ecotoxicology, field team oversight
Dr. Robert George	SSC Pacific 53475 Strothe Rd. San Diego, CA 92152	Tel: (619) 553-2776 Fax: (619) 553-6305 george@spawar.navy.mil	Co-PI, Technical, chemistry, field team
Mr. Bill Wild	SSC Pacific 53475 Strothe Rd. San Diego, CA 92152	Tel: (619) 553-2781 Fax (619) 553-6305 bill.wild@navy.mil	Co-PI, Technical, field team
Dr. Guilherme Lotufo	USACE Engineer Research Development Center (ERDC) 3909 Halls Ferry Rd. Vicksburg, MS 39180	Tel: (601) 634-4103 Guilherme.Lotufo@usace.army.mil	Co-PI, Technical and field work
Dr. Jason Belden	Oklahoma State University Dept of Zoology 501 Life Sciences West Stillwater, OK 74078	Tel: (405) 744-1718 jbelden@okstate.edu	Co-PI, Analytical chemistry
Dr. David Smith	USACE Engineer Research Development Center (ERDC) 3909 Halls Ferry Rd. Vicksburg, MS 39180	Tel: (601) 634 4267 Cell: (601) 529 6167 david.l.smith@usace.army.mil	Co-PI, Research Ecologist, Flume study oversight
Mr. Jim Biedenbach	USACE Engineer Research Development Center (ERDC) Vicksburg, MS	James.M.Biedenbach@usace.army.mil	Flume study technical support/logistical support
Mr. Daniel Waddill	NAVFAC Atlantic Attn: Code EV31 6506 Hampton Boulevard Norfolk, VA 23508-1278	Tel: (757) 322-4983 dan.waddill@navy.mil	Head of Vieques Restoration Section
Mr. Daniel Hood		Tel: (757) 322-4630 daniel.r.hood@navy.mil	Remedial Project Manager Vieques Restoration Section
Mr. Kevin Cloe		Tel: (757) 322-4736 kevin.cloe@navy.mil	Remedial Project Manager Vieques Restoration Section
Mr. Mike Green		Tel: (757) 322-8108 mike.green@navy.mil	Explosive Ordnance Detection, Vieques Restoration Section
Ms. Madeline Rivera	Navy Field Office PO Box 1532 Vieques, PR 00765	Tel: (787) 741-4792 madeline.rivera@navy.mil	Vieques Site Manager Vieques Restoration Section
Ms. Diane Wehner	NOAA Office of Response and Restoration 290 Broadway Rm 2059 New York, New York 10007	Tel: (240) 338-3411 diane.wehner@noaa.gov	NOAA Office of Response and Restoration
Mr. Brett Doer	Environmental Services Bus Grp CH2M HILL 5701 Cleveland Street, Suite 200 Virginia Beach, VA 23462	Tel: (757) 671-6219 Fax: (703) 376-5977 Cell: (757) 348-8409 brett.doerr@ch2m.com	Senior Project Manager/ Hydrogeologist, Dive Plan

Point of Contact Name	Organization Name Address	Phone Fax E-mail	Role in Project
Ms. Marienne Colvin	SSC Pacific 53475 Strothe Rd. San Diego, CA 92152	Tel: (619) 553-2788 Fax: (619) 553-6305 mcolvin@spawar.navy.mil	Technical support/logistics
Daniel Rodriguez	U.S. Environmental Protection Agency Vieques Field Office PO Box 1537 Vieques, Puerto Rico, 00765	Tel: (787) 741-5201 Rodriguez.Daniel@epamail.epa.gov	EPA Remedial Project Manager
Dr. Lisamarie Carrubba	NOAA Fisheries Caribbean Field Office, PRD P.O. Box 1310 Boqueron, PR 00622	Tel: (787) 851-3700 lisamarie.carrubba@noaa.gov	NOAA Fisheries
Wilmarie Rivera	Puerto Rico Environmental Quality Board P.O. Box 11488 San Juan, PR 00910	Tel: (787) 767-8181 wilmarierivera@jca.gobierno.pr	Federal Facilities Coordinator
Sindulfo Castillo	USACE Antilles Office, Regulatory Section 400 Fernández Juncos Ave. San Juan PR 00901- 3299	Tel: (787) 729-6905 Sindulfo.Castillo@usace.army.mil	Nationwide Permitting
Craig Lilyestrom	Department of Natural and Environmental Resources P.O. Box 366147 San Juan, Puerto Rico 00936	Tel: (787) 999-2200 x2615 craig.lilyestrom@drna.gobierno.pr	Director, Marine Resources; DNER Permit for Biota Collection
Nilda Jimenez	Department of Natural and Environmental Resources P.O. Box 366147 San Juan, Puerto Rico 00936	njimenez@drna.gobierno.pr	DNER Permit for Biota Collection

ESTCP Office
4800 Mark Center Drive
Suite 17D08
Alexandria, VA 22350-3605
(571) 372-6565 (Phone)
E-mail: estcp@estcp.org
www.serdp-estcp.org