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ADMINISTRATIVE INFORMATION

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The 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 MC on the marine environment, which has resulted in costly risk characterization efforts (e.g., NAVFAC, 2011; USACE, 2012; UH, 2014a; and UH 2014b) and could lead to more resource-intensive remediation efforts. Although underwater UWMM have the potential to corrode, breach, and leak munitions constituents (MCs) such as 2,4,6-trinitrotoluene (TNT) and 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 very low (ng/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, and 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 MC 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) 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 underwater military munitions (UWMM) sites.

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

Exposure data from the proposed validation efforts were then compared with existing toxicity criteria (Lotufo et al., 2017) to assess potential for ecological risk of UWMM associated with the data derived from the field. The technology user's guide is appended to this report, and will be made separately available to Department of Defense (DoD) end users, regulators, and commercial laboratories for POCIS employment at such sites.

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 (Table 1-1) 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, Debenest, and Delmas, 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).

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
1	POCIS will detect MC in positive control field deployment (Gulf Breeze, FL).	In controlled field study, POCIS analyzed for TNT, ADNTs, DANTs, and RDX.	Detectable MC concentrations in POCIS.	Met. In controlled field study with Composition B explosive fill material, MC detected at 9–103 ng/L 0.3 to 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. Composition B flume studies showed that POCIS TWA concentrations were 19–44% and ≤6% higher than TWA concentrations derived for multiple grab samples. In the positive control field study, POCIS data were more meaningful, as MC 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, the average TNT concentration from the two grab samples (5,984 ng/L) was only 11% higher than the average for POCIS (5,304 ng/L).

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
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 time-weighted average 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 grabs.
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 while 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 reported as non-detects (detection frequency = 0); contrastingly, POCIS-derived TWA concentrations were reported for 12 of 20 stations (detection frequency = 60%). For Vieques field validation, RDX in initial grab samples were detected for 3 of 15 stations (detection frequency = 20%), while for final grab samples RDX was reported as non-detect for all stations (detection frequency = 0). Contrastingly, POCIS-derived TWA concentrations for 11 of 14 stations (detection frequency = 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 (one sample lost in lab).

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
6	Quality control and Quality assurance meet technology requirements	Site- and/or experiment-specific sampling and analysis plans (e.g., demonstration plan) will be developed.	Per sampling and analysis plans, trip and laboratory blanks less than quantitation limit, laboratory spikes within 25% of expected, chain of custody and sample control procedures followed.	Met. Trip blanks and laboratory blanks were below quantitation limits. All chain of custody and sample control procedures were met. Extraction of POCIS and SPE of water samples were always less than 25%. A few analytes in tissue and sediment had recoveries up to 30% lower. See Appendix E for more details.
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 prep 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. They indicated the deployment and recovery went well, but they noted the design was labor intensive, and costly in comparison to grab sampling, which can be done in a single field effort without divers. We agree with this conclusion if assuming that integrated sampling will not provide added value, but complexity is expected to be 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 only technology that detected MC in positive control study, and had a higher frequency of detects compared to grab sampling at Vieques. 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 help convince the Vieques public that samplers were placed in representative locations.

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
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 Munitions Response 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 site.

PERFORMANCE EVALUATION

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

Performance objective 1 was the verification that POCIS could detect munitions constituents (MCs) in a positive control field study at a clean site. Following permit approvals, 15 grams of Composition 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.

Performance Objective #2: Accurate Quantification of Time-Weighted Average 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 Composition B flume study, the positive control field study, and the Vieques field validation study. Composition B flume-deployed POCIS estimated TWA water concentrations for TNT and RDX that were similar to averaged concentrations generated using multiple grab TWA concentrations. The highest ratio of the POCIS-derived and the grab-sample-derived averages was only 1.44. In the positive control field study, MC concentration successfully determined using POCIS (TWA water concentrations 0.3 to 2 m from source, 9–103 ng/L for TNT, and 9–97 ng/L for RDX) could not be compared to discrete-sampling-derived concentrations, as grab water samples resulted only in non-detects. When considering the QL for grab samples (50 and 120 ng/L for TNT and RDX, respectively), grab sample data provide some level of validation of the POCIS-derived data. In the Vieques field validation study, one 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 (5,984 ng/L) at the station was only 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. POCIS-derived average RDX concentrations ranged narrowly from 5 to 13 ng/L (average = 8 ng/L) for 11 stations

with detectable concentrations. Only three stations had detectable concentration from grab samples during the initial period, and all stations had concentrations reported as non-detects for the final period. The three reported concentrations for the initial period were 24, 26 and 51 ng/L. When considered along with the non-detects reported for the final period, average concentrations estimated using POCIS and two grab samples were similar. Overall, data from grab samples validated the data obtained using POCIS for all the flume and field studies.

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.

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

Performance objective 4 was the demonstration that the POCIS sampler would detect MC at levels substantially lower than achievable using typical grab sampling methods. 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) which was consistent for all grab water samples. Detection limits for POCIS-derived TWA concentrations and grab water samples are generally comparable when the volume of water volume of water cleared of MCs' for both methods is comparable (e.g., 3-week POCIS deployment and 10 L of grab water sample). For the Comp. B positive control study, the concentrations of TNT and RDX in grab samples taken at three different time points adjacent to the source were reported as non-detects; in contrast, POCIS-derived TWA concentrations were reported for 12 out of 20 stations, including those more distant from the source than the point of grab water sampling. For 12 stations out of 15 in the Vieques field validation study, the concentrations of RDX in grab samples were reported as non-detects; in contrast, POCIS-derived TWA concentrations were reported for 8 out those 12 stations. For the Vieques field validation study, the concentrations of RDX in the initial grab samples were reported as non-detects for 3 out of 15 stations (detection frequency = 20%), while for final grab samples RDX was reported as non-detects for all stations (detection frequency = 0). In contrast, POCIS-derived TWA concentrations were reported for 11 out of 14 stations (detection frequency = 79%). Despite POCIS having a higher frequency of detection than grab samples at Vieques, the detection levels for both grab sampling and for POCIS were below regulatory screening levels and both sampling methods clearly showed no unacceptable risk. Therefore, the grab samples and POCIS are expected to be of equal value for CERCLA risk assessment.

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. A total of 20, 51, and 30 POCIS canisters (each containing three 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 method detection limits, 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 (Section 2.2; Appendix D) 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: Quality Control and Quality Assurance

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

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. 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 to 1,000,000 times lower than hazardous concentrations to 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 clearly showed no unacceptable risk. Therefore, the grab samples and POCIS are expected to be of equal value for CERCLA risk assessment at that site.

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 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 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 don't degrade (e.g., freeze or extract samples daily). Laboratory feedback indicated that processing of POCIS in comparison with standard solid-phase extraction (SPE) of grab water samples was negligible.

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. 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), 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.

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. 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 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 the 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 would produce similarly integrative samples (see Section 7), 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 (see Section 7). In addition, POCIS sampling is expected to directly address sentiment from those concerned with UWMM as sources of contamination who perceive grab sampling may take place at the wrong time, in the wrong place, 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 leave in place versus a removal decision-making processes.

CONCLUSION

Based on results from laboratory, positive field control, and UWMM site field validation efforts, we conclude 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 quantitation limit occurred at only 1 of 30 stations, with the relatively large value (5.3 µg/L) quantified immediately adjacent to a breached munition. 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. Note 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 to 10 L would more closely represent the volume cleared by the POCIS in a 2- to 3-week deployment and result in more comparable detection limits. Finally, note that although POCIS data have the potential to be more informative as integrative samplers, the field validation at Vieques showed no ecological risk with both POCIS and traditional sampling technologies.

ACRONYMS

2,4-DNT	2,4-dinitrotoluene
2,4,6-TNT	2,4,6-trinitrotoluene
2,4-DANT	2,4-diamino-6-Nitrotoluene
2,6-DANT	2,6-diamino-4-Nitrotoluene
2,6-DNT	2,6-dinitrotoluene
2-ADNT	2-amino-4,6-dinitrotoluene (2-ADNT)
4-ADNT	4-amino-2,6-dinitrotoluene (4-ADNT)
ADNT	Aminodinitrotoluene
ADV	Acoustic doppler velocimetry
AFWTA	Atlantic Fleet Weapons Training Area
ATSDR	Agency for Toxic Substances & Business Registry
BIP	Blow in Place
BRAC	Base Realignment and Closure
BSS	Bahia Salina del Sur
CERCLA	Comprehensive Environmental Response, Compensation, & Liability Act
Comp B	Composition B (39.5% TNT, 59.5% RDX, 1% wax)
CSM	Conceptual Site Model
DANT	Diaminonitrotoluene
DDT	Dichlorodiphenyltrichloroethane
DMM	Discarded Military Munitions
DNB	1,3-dinitrobenzene
DOC	Dissolved Organic Carbon
DoD	Department of Defense
DOI	United States Department of Interior
ECA	Eastern Conservation Area
EMA	Eastern Maneuver Area
EOD	Explosive Ordnance Disposal
EPA	Environmental Protection Agency
ERA	Expanded Range Assessment
ERM	Environmental Resource Management
ER,N	Environmental Restoration, Navy
ESA	Endangered Species Act
ESTCP	Environmental Security Technology Certification Program
FFA	Federal Facilities Agreement
FS	Feasibility Study
FUDS	Formerly Used Defense Site
FY	fiscal year
GC/MS	Gas Chromatography/Mass Spectrometry
GED	EPA Gulf Ecology Division
GMI	Geo-Marine, Incorporated
GPS	Global Positioning System
HLB	Hydrophilic-lipophilic balance (POCIS sorbent)
IR	Installation Restoration
K_{ow}	Octanol-water partition coefficient
LIA	Live Impact Area
LIP	Leave in Place

LOD	Low Order Detonation
MC	Munitions constituents
MD	Munitions Debris
MDL	Method Detection Limit
MEC	Munitions and explosives of concern
MLW	Mean low water
MMRP	Military Munitions Response Program
MRP	Munitions Response Program
MRS	Munitions Response Site
NASD	Naval Ammunition Support Detachment
NAVFAC	Naval Facilities Engineering Command
NESDI	Navy's Environmental Security Development to Integration Program
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOSSA	Naval Ordnance Safety and Security Activity
NPL	National Priorities List
OE	Ordnance and explosives
OSU	Oklahoma State University
PAH	Polycyclic aromatic hydrocarbon
PAOC	Potential area of concern
PCB	Polychlorinated biphenyl
PES	Polyethersulfone
POC	Point of Contact
POCIS	Polar Organic Chemical Integrative Sampler
PRC	Performance Reference Compound
PREQB	Puerto Rico Environmental Quality Board
PRDNER	Puerto Rico Department of Natural and Environmental Resources
PSD	Passive Sampling Device
QAPP	Quality Assurance Project Plan
QL	Quantitation Limit
RA	Remedial Action
RAD	Remedial Action Objectives
RCRA	Resource Conservation and Recovery Act
RD	Remedial Design
RDX	Hexahydro-1,3,5-trinitro-s-triazine (also Royal Demolition Explosive)
RFI	RCRA Facility Investigation
RI	Remedial Investigation
ROD	Record of Decision
ROV	Remotely Operated Vehicle
R_s	Sampling Rate
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Plan
SI	Site Inspection
SIA	Surface Impact Area
SSS	Side-scan sonar
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TOC	Total Organic Carbon
TSS	Total Suspended Solids

TWA	Time-weighted average
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
USN	United States Navy
UXO	Unexploded ordnance
UWMM	Underwater Military Munitions
VNTR	Vieques Naval Training Range
WAA	Wide Area Assessment

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1. INTRODUCTION

1.1 BACKGROUND

The 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 (MC) on the marine environment, which has resulted in costly risk characterization efforts (e.g., NAVFAC; 2011, USACE, 2012; UH, 2014a, UH, 2014b) and could lead to more resource intensive remediation efforts. Although underwater UWMM have the potential to corrode, breach, and leak MC, 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, Kroger, Leisle, and Feldpausch, 2010; Rosen and Lotufo, 2010; Wang, George, Wild, and Liao, 2011), 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, and 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, Rosen, Wild, and Carton 2013). Regardless, one of the primary outcomes of a recent SERDP workshop (SERDP, 2010) was the need to conduct field data collections at (preferably worst-case) UWMM sites.

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 integrative 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 reduce numbers of analyses required, and provide 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 for which to evaluate ecological risk associated with MC exposure to environmental receptors. Without such data, the DoD would lack methodological sensitivity and meaningful data that is essential 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 vs. 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 MC at environmentally relevant concentrations in laboratory-based studies under the Navy's Environmental Sustainability Demonstration 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) 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 underwater military munitions (UWMM) sites

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

Exposure data from the proposed validation efforts were then compared with existing toxicity criteria (Lotufo et al., 2017) to assess potential for ecological risk of UWMM associated with the data derived from the field. For more information see a Technology User's Guide, Appendix H. The Technology User's Guide will be made separately available to DoD end users, regulators, and commercial laboratories for POCIS employment at such sites.

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 more than 400 sites, totaling more than 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, MR Program, personal communications). The inventory includes sites that date back to the 18th 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 have largely been unresolved due to insufficient clarity regarding analytical sensitivity to detect potentially toxic MC. Therefore, we believe that 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) vs. removal, or blow in place (BIP).

Since Vieques is a Superfund site, the regulatory drivers for addressing MC underwater at Vieques, Puerto Rico, operates at 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., polar organic chemical integrative sampler (POCIS) and Chemcatcher®).

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 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, Debenest and Delmas, 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).

Figure 2-1. POCIS sampler (left) and commercially available field holder and canister for POCIS (right).

The POCIS was developed to sample a wide variety of organic compounds with log K_{ow} of 3.0 or less. Because TNT, RDX, and their major degradation products, have relatively low log K_{ow} values of approximately 2.0 or less, and because the POCIS has been successfully used in marine environments (Harman, and Vermeirssen 2012; Munaron, Tapie, Andral, and Gonzalez, 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 Navy's Environmental Sustainability Development to Integration (NESDI) Program, Project #465. The POCIS consists of a receiving phase (sorbent) sandwiched between two polyethersulfone (PES) microporous membranes with ~ 0.1 µm pore size (Alvarez et al., 2004; Figure 2-2). The sampler is compressed together using two stainless steel rings (interior diameter 51–54 mm), which provides an exposure surface area of 41–46 cm^2. The samplers are available commercially from Environmental Sampling Technologies (EST), which use the widely used Oasis® hydrophilic–lipophilic balance (HLB) sorbent, which worked well under NESDI Project #465 Belden et al., 2015).

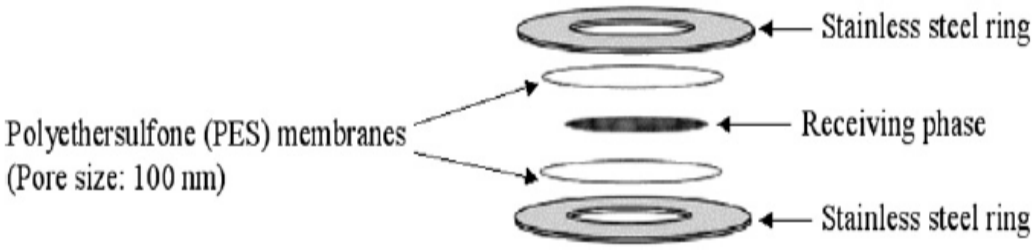

Figure 2-2. Disassembled view of the POCIS (from Morin, Random, and Coquery, 2012).

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, Vermeirssen, Helms, and Metcalfe, 2010; Mazzella, Debenest, and Delmas, 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 polyethersulfone 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 and Vermeirssen, 2012, and Morin, Meige, Random, and Coquery, 2012). On a relative scale, other variables, including temperature, nutrients, dissolved organic carbon, salinity, and biofouling have been found to have less impact on R_s.

Deployment of samplers at UWMM sites will ideally be attached to a weight on the sea floor, and placed either adjacent to suspected leaking ordnance or in a grid-shaped fashion over a given sampling area (to be verified in this projects Demonstration Plan following discussion with NAVFAC points of contact (POC)s, with evaluation and concurrence by the Naval Ordnance Safety and Security Activity (NOSSA) and Navy Explosive Ordnance Disposal (EOD) technicians. A generic visual 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.

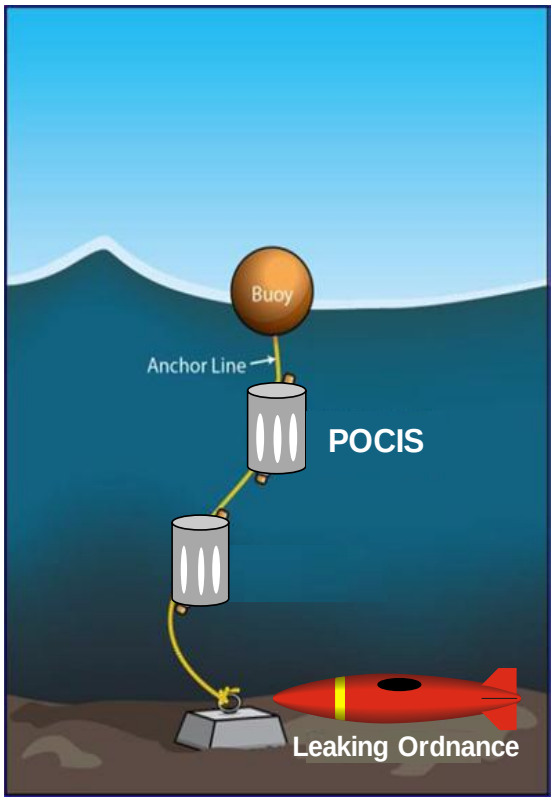

Figure 2-3. Generalized diagram of how POCIS might be incorporated into site characterization at a UWMM site.

U.S. Patent 6,478,916 B2 (Petty et al., 2002)

Commercially available from EST Inc. for pharmaceuticals and polar pesticides (2003)

U.S. Coast Guard (USGS) POCIS Guidance (Alvarez, 2010)

Critical review papers (Harman, and Vermeirssen, 2012; Morin et al., 2012

NESDI Project #465: Calibration/lab Demo for munitions constituents (MC); (2011–2014)

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 current POCIS technology.

2.2 TECHNOLOGY DEVELOPMENT

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 expanded on in Appendices B, C, and D.

2.2.1 Positive Control (Composition B) Field Evaluation

Positive control study. An in-depth reporting of this effort (Task 1) is provided in Appendix B. In brief, this study examined the ability for POCIS to detect and quantify common conventional munitions constituents (MC), including trinitrotoluene (TNT), aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs), dinitrotoluene (DNT), and trinitrohexahydro-s-triazine (RDX) in a field setting with a known MC source. POCIS were deployed at varying distances from fragments (15 g total mass) of the explosive formulation Composition B (39.5% TNT, 59.5% RDX, and 1% wax binder) in an embayment of Santa Rosa Sound (Florida, USA) adjacent to the USEPA's Gulf Ecology Division. POCIS-derived time-weighted averaged (TWA) estimated water concentrations from a 13-day deployment ranged from 9–103 ng/L for TNT and RDX outside the source canister, with concentrations decreasing with increasing distance from the source to below quantitation limits (5–7 ng/L) at stations >2 m away from the source (Figure 2-5). The results of the positive control study provide critical field validation of the sensitivity and integrative advantages of POCIS for munitions constituents, as field validation at an actual UWMM site in a coastal area does not guarantee exposure due to multiple uncertainties associated with munitions.

Biofouling study. Moderate biological fouling observed on POCIS membranes after 13-days during the positive control study led to a subsequent experiment to investigate the potential effects of biofouling on sampling rate (R_s) for MC. Briefly, following conditioning periods of 0, 7, 14 or 28 days at the same field site in Santa Rosa Sound, FL, during which different degrees of biofouling was established on the POCIS membranes, POCIS were transferred to aquaria spiked with trace quantities of multiple MC for a 7-days uptake experiment. No significant differences in R_s were observed among the different fouling time periods (Figure 2-6). Mass (means and standard deviations) of MC accumulated by POCIS samplers in 7-day spiked laboratory exposures post-field deployment of samplers at Santa Rosa Sound, FL for 0 to 28 days. No significant differences among treatments were observed for any analyte.although mass of fouling organisms on the membranes was statistically greater at the 28-day field exposure compared to shorter field exposure time points, which also corresponded with visual observations (Figure 2-7). This study verified the high sensitivity and integrative nature of POCIS for dominant conventional MC in estuarine environments, and provided rationale for moving forward with the site demonstration at Vieques. The details associated with this follow on study are provided in Appendix B, and are in the process of being prepared for publication.

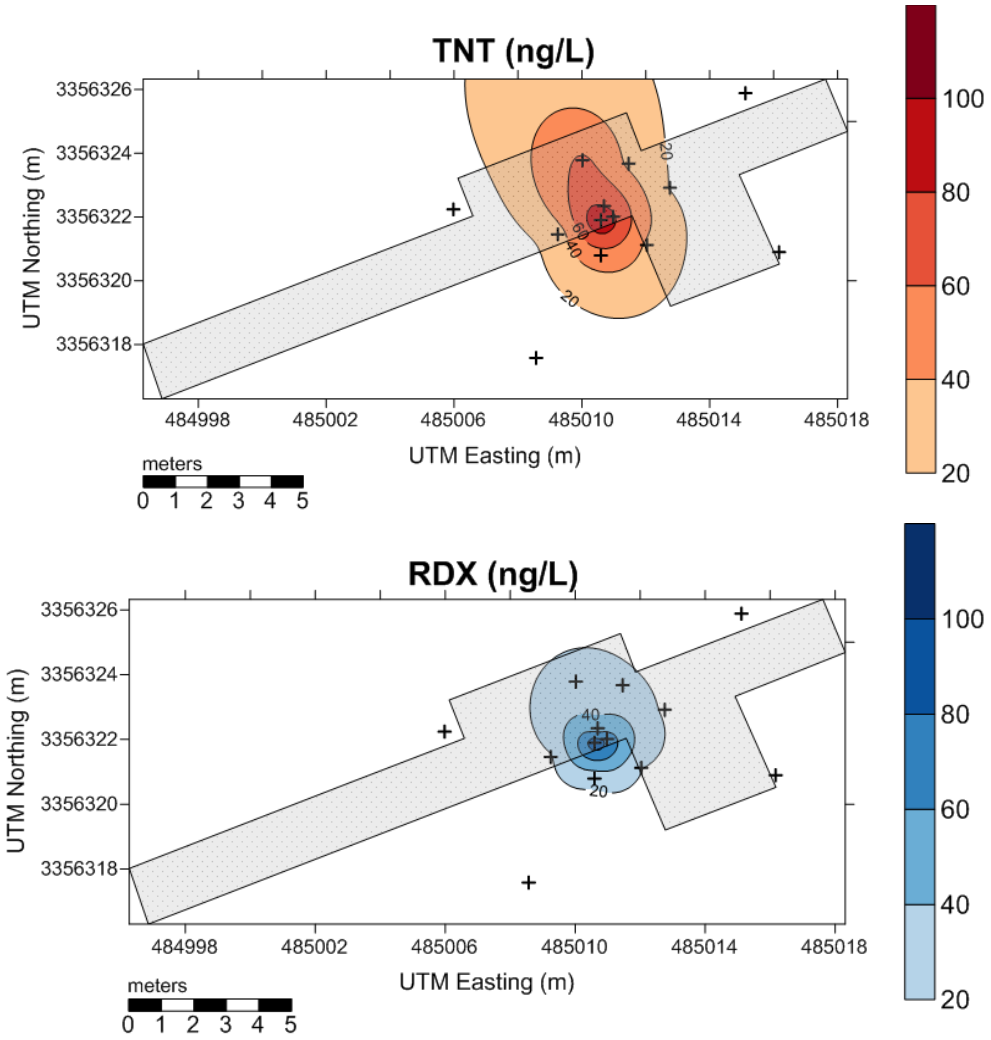

Figure 2-5. POCIS-derived water concentrations for TNT and RDX from positive control field study.

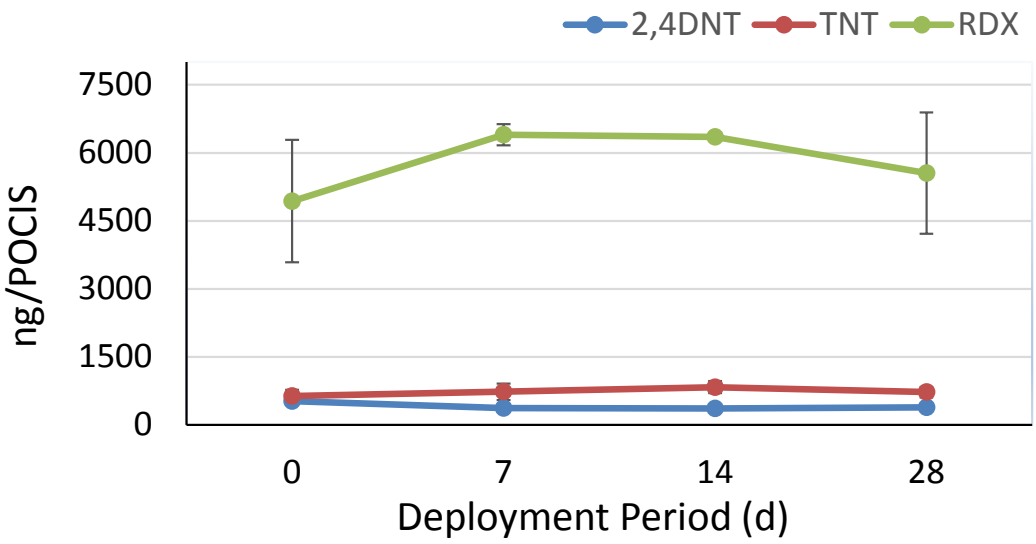

Figure 2-6. Mass (means and standard deviations) of MC accumulated by POCIS samplers in 7-day spiked laboratory exposures post-field deployment of samplers at Santa Rosa Sound, FL, for 0 to 28 days. No significant differences among treatments were observed for any analyte.

Figure 2-7. Representative pictures of POCIS membranes upon initiation of 7-day MC spike laboratory experiment following deployment at Gulf Breeze East Dock (from left to right), for 0, 7, 14, and 28 days during July 7 to August 4, 2015.

2.2.2 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 flume (Figure 2-8). In addition to investigating the influence of flow rate (range 7–30 cm/s) on POCIS sampling rate (R_s), we 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, described in substantially more detail in Appendix C, 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 Rs 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.

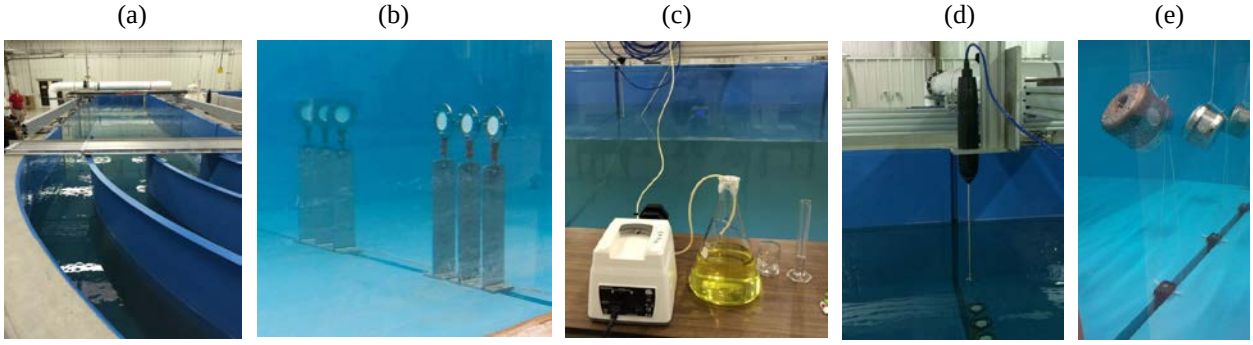

Figure 2-8. Flume studies to assess flow-related effects on uptake by POCIS. From left to right: (a) partial view of the 113,000-L flume, (b) POCIS in multiple positions and orientations, (c) MC spike, (d) precise flow velocity measurements with acoustic Doppler velocimetry (ADV), and (e) POCIS in protective canisters.

Table 2-1. Regression equations (and R^2) for each of four MC for both uncaged and caged POCIS.

MC	POCIS Configuration	
	Uncaged	Caged
TNT	0.081fr + 0.014 (0.93)	0.018fr - 0.05 (0.89)
2,4-DNT	0.003fr + 0.052 (0.82)	0.004fr + 0.08 (0.98)
2,6-DNT	0.003fr + 0.065 (0.79)	0.004fr + 0.007 (0.98)
RDX	0.005fr + 0.314 (0.46)	0.008fr + 0.27 (0.53)

Fr = flow rate

2.2.3 Composition 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 Composition B fill, simulating a low order detonation (LOD), and scenario 2 representing the release

of MC from Comp B through a small hole, simulating a recently breached munition (Figure 2-9). 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 days for the exposed fill experiment and 13 days 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 (Figure 2-10). 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 a LOD, among other scenarios. The full details of this series of experiments are provided in Appendix D.

For TNT, the POCIS estimated TWA concentrations were 1.19 and 1.44 times higher than those derived from grab samples for scenarios 1 and 2, respectively. For RDX, POCIS estimated TWA concentrations were at most 6% higher than those derived from grab samples for both scenarios. The overall good agreement in estimating water concentration from POCIS and with measured concentrations in water samples was also previously reported from experiments where Comp B was deployed as an open source or encased with only a 0.125-inch hole allowing diffusion (Belden et al., 2015), further confirming the expected accuracy of using POCIS for determining TWA concentrations of MC released to the surrounding water from UWMM. Results from our study corroborate those from previous investigations (Terzopoulou and Voutsa, 2016; Poulier et al., 2015; Coes et al., 2014) that demonstrated that POCIS provide reliable temporal integration of changing environmental concentrations that would require frequent grab sampling events potentially requiring large volumes of water to obtain comparable temporal integration. In addition, POCIS and POCIS-style samplers sequester residues from episodic events that may not always be detected with grab sampling (Morrison and Belden, 2016; Bueno et al., 2016).

Figure 2-9. Cleaved munition surrogate produced from intact full-surrogate 155-mm replica loaded with Comp B fragments as an open source (left and center) and encased within a 1-cm hole (right).

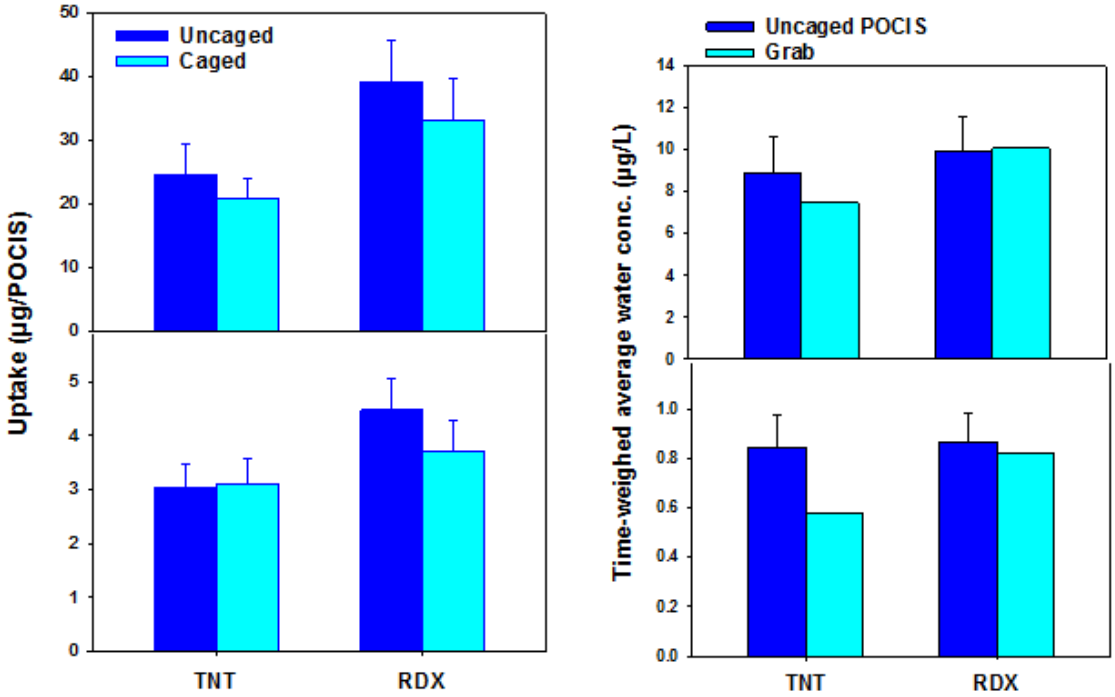

Figure 2-10. (left) Comparison of MC uptake in caged and uncaged POCIS in the fully exposed (top) and encased (bottom) experiments; (right) comparison of TWA water concentrations between uncaged POCIS and multiple grab samples for fully exposed (top) and encased (bottom) experiments.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.3.1 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 over 300 different polar organic chemicals, and are commercially available. They 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.

2.3.2 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 sampling rate (*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 *Rs* (Harman, Allen, and

Vermeirssen, 2012). Efforts to improve the quantitative ability of POCIS are ongoing, including a recently completed SERDP SEED project (ER-2542) that reported clear advantages towards the use of nylon mesh to reduce the influence of flow on MC uptake and/or the incorporation of Micro Flow 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 to execute successfully.

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), and are shown in Table 3-1.

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
1	POCIS will detect MC in positive control field deployment (Gulf Breeze, FL).	In controlled field study, POCIS analyzed for TNT, ADNTs, DANTs, and RDX.	Detectable MC concentrations in POCIS.	Met. In controlled field study with Composition B explosive fill material, MC detected at 9-103 ng/L 0.3 to 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. Composition B flume studies showed that POCIS TWA concentrations were 19-44% and ≤6% higher than TWA concentrations derived for multiple grab samples. In the positive control field study, POCIS data were more meaningful, as MC 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, the average TNT concentration from the two grab samples (5,984 ng/L) was only 11% higher than the average for POCIS (5,304 ng/L).
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 time-weighted average 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 grabs.

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

Quantitative Performance Objectives				
#	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 while 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 reported as non-detects (detection frequency = 0); contrastingly, POCIS-derived TWA concentrations were reported for 12 of 20 stations (detection frequency = 60%). For Vieques field validation, RDX in initial grab samples were detected for 3 of 15 stations (detection frequency = 20%), while for final grab samples RDX was reported as non-detect for all stations (detection frequency = 0). Contrastingly, POCIS-derived TWA concentrations for 11 of 14 stations (detection frequency = 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 lab).

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
6	Quality control and Quality assurance 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 quantitation limit, 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 quantitation limits. All chain of custody and sample control procedures were met. Extraction of POCIS and SPE of water samples were always less than 25%. A few analytes in tissue and sediment had recoveries up to 30% lower. See Appendix E for more details.
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 prep 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. They indicated the deployment and recovery went well, but they noted the design was labor intensive, and costly in comparison to grab sampling, which can be done in a single field effort without divers. We agree with this conclusion if integrated sampling does not provided added value, but complexity is comparable if autosampling and multiple trips to the site are desired for an integrated sample.

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

Quantitative Performance Objectives				
#	Performance Objective	Data Requirements	Success Criteria	Results
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 only technology that detected MC in 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 help convince 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 Munitions Response 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 site.

3.1 QUANTITATIVE PERFORMANCE OBJECTIVES

3.1.1 Performance Objectives #1: Detection of MC in Controlled Field Study

3.1.1.1 Description

As there is considerable uncertainty with respect to the presence of MC in the water column at any given time at UWMM sites, a positive control field study was conducted at the East Dock at the USEPA Gulf Ecology Division in the Santa Rosa Sound (Gulf Breeze, FL) to validate the POCIS technology in a field setting. A known quantity (15 g total mass) of small fragments of Composition B (39.5% TNT, 59.5% RDX, 1% wax) were deployed as a source of MC to the water column. Details on this study are provided in Section 2.2 and in Appendix B.

3.1.1.2 Data Requirements

A total of 20 POCIS sampling canisters were strategically placed around the source at varying distances (i.e., 0.3, 2, and 5 m) over a 13-day exposure period. Oysters (*Crassostrea virginica*) were deployed for the same time period, and grab water samples were collected at three time points (Days 1, 6, and 13) during the exposure. TNT, ADNTs, and RDX were targeted for all matrices.

3.1.1.3 Success Criteria

Detectable MC concentrations in POCIS.

Extent Success Criteria Were Met

In the controlled field study, MC ranged from 9-103 ng/L (TWA concentration) between 0.3 and 2 m from the Composition B source. Concentrations were highest at the 0.3 m sampling locations, lower at 2 m, and not detectable at 5 m sampling points. All tissue and grab water concentrations were below their associated method detection limits (Section 2.2, Appendix B). TNT and RDX were detected at 0.3 and 2 m, but ADNT concentrations were only detected in the source canister, where TNT and RDX were an order of magnitude higher in concentration than outside the source canister.

3.1.2 Performance Objective #2: Accurate Quantification of Time-Averaged MC Concentrations

3.1.2.1 Description

Environmental conditions such as flow rate, salinity, temperature, and biofouling can cause variations in the sampling rate and thus influence the accuracy of time-averaged MC concentrations determined using POCIS, for which sampling rates determined in laboratory calibration experiments. Despite uncertainties associated with both methodologies, comparison of time-weighted average concentrations derived using POCIS and discrete sampling of the water column is expected to provide reasonable verification of the accuracy associated with the POCIS technology.

3.1.2.2 Data Requirements

Simultaneous collection of POCIS-derived and discrete-sampling-derived concentrations under actual field conditions or field conditions simulated in a flume.

3.1.2.3 Success Criteria

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.

Extent Success Criteria Were Met

For the Composition B flume studies, the POCIS estimated TWA concentrations were 1.19 and 1.44 time higher than those derived from multiple grab samples for open exposed and 1 cm hole experiments, respectively (see Section 2.2; Appendix D). For RDX, POCIS estimated TWA concentrations were < a factor of 1.06 higher than those derived from grab samples for open and holed experiments (Figure 2-10). Overall, data from grab samples fully validated the data obtained using POCIS for the flume field simulation study. The good agreement in estimating water concentration from POCIS and with measured concentrations in water samples was also previously reported from experiments where Comp B was deployed as an open source or encased with only a 0.125-inch hole allowing diffusion (Belden et al., 2015), further confirming the expected accuracy of using POCIS for determining TWA concentrations of MC released to the surrounding water from UWMM.

In the positive control field study, MC concentration successfully determined using POCIS (TWA water concentrations 9-103 ng/L from 0.3 to 2 m from source) could not be compared to discrete-sampling-derived concentrations as grab water samples resulted only in non-detects. It was anticipated that grab samples might be below detection at the site based on the ultra-low concentrations expected to be in the water in the vicinity of the Composition B source, showing the

value of the time-integrations capability of POCIS, which incrementally accumulated MC dissolving from the source over the 13-day exposure.

In the Vieques field validation study, the average TNT concentration from the two grab samples (5,984 ng/L) was only 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. The minimal differences between the grab and time-weighted averaged concentrations suggest that the breaches may have been a continuous source to the area immediately where water sampling occurred. POCIS-derived average RDX concentrations ranged narrowly from 5 to 13 ng/L (average = 8 ng/L) for 11 stations with detectable concentrations. Only three stations had detectable concentrations from grab samples during the initial period, and all stations had concentrations reported as non-detects for the final period. The three reported concentrations for the initial period were 24, 26, and 51 ng/L. When considered along with the non-detects reported for grab samples taken at end of POCIS deployment (the final period), average concentrations estimated using POCIS and average concentration derived using two grab samples were similar. Overall, data from grab samples fully validated the data obtained using POCIS for the Vieques field study.

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

3.1.3.1 Description

The potential for current velocity to influence sampling has been previously investigated or reviewed (e.g., Li et al., 2010; Charlestra et al., 2012; Harman et al., 2012; Di Carro, Bono, and Magi, 2013) and generally indicated that increasing current velocities cause increases in sampling rate by less than two-fold. Comparison of TWA concentrations derived using POCIS and discrete-sampling of the water column under varying current velocities in a flume provided reasonable verification of the influence of current velocity on the accuracy of POCIS measurements.

3.1.3.2 Data Requirements

Sampler uptake and discrete-sampling data derived using varying current velocities in flume.

3.1.3.3 Success Criteria

Development of sampling rates and TWA concentrations under controlled experimental conditions in a flume.

Extent Success Criteria Were Met

A positive linear relationship between current velocity and sampling rate for POCIS was established for multiple MC, useful for correcting sampling rate based on current velocity. From the regression equations derived, simple calculations can be used to correct for current velocity if such measurements are made at the field site. In this project, a Nortek™ current profiler was used at Vieques to calculate the optimum sampling rate based on measured flow. Two different explosive fill encapsulation scenarios showed highly comparable TWA concentrations for POCIS and multiple grabs. See Section 2.2 and Appendices C and D for full detail on the flume experiments.

3.1.4 Performance Objective #4: Detection OF MC at Levels Substantially Lower than Achievable for Water Samples

3.1.4.1 Description

Discrete-sampling of the water column at UWMM sites has resulted in the vast majority of samples with concentrations below the level of detection (Lotufo et al., 2017). The use of POCIS technology is expected to concentrate contaminants present at low levels in the water column. Because relevant chemicals are strongly bound to the sorbent phase, no significant losses of residues during the exposure period are expected, resulting in optimal quantitation of sequestered chemicals. The continuous sampling provided by POCIS may result in detection at levels lower than those obtainable by quantifying contaminants in the volume (e.g., 1L) of water typically collected during grab sampling efforts.

3.1.4.2 Data Requirements

Conduct field and flume studies using discrete (i.e., grab) sampling alongside integrative POCIS samplers.

3.1.4.3 Success Criteria

The following criteria were successfully met.

1. Quantitation limit (QL) for POCIS (as TWA concentrations) substantially lower than quantitation limit in 1 L discrete water samples.

2. POCIS continuous sampling over time at field sites will result in MC detection while MC concentrations in corresponding discrete water samples may be below detection.

3. POCIS continuous sampling over time at field sites will result in higher frequency of detection of MC compared to grab samples.

Extent Success Criteria Were Met

Details of extent success criteria met are as follows:

1. The QL for POCIS-derived TWA concentrations were consistently lower than those derived for discrete samples (Table 3-2). Lower detection limits were achieved using POCIS sampling because the estimated volumes of water cleared of MC during the deployment time (4 to 12 L for TNT, and 11 to 24 L for RDX) (Table 3-2) were substantially greater than the volume (1 L) consistently collected for grab water samples. Sampling and concentrating 10 L of water instead of 1 L would have generally resulted in lower QL for grab samples than for POCIS-derived TWA (Table 3-2). In summary, the detection limits for POCIS-derived TWA concentrations are substantially greater than for 1 L discrete water samples, but detection limits for POCIS-derived TWA concentrations and grab water samples are generally comparable when the volume of water volume of water cleared of MC for both methods is comparable (e.g., 3-week POCIS deployment and 10 L of grab water sample).

Table 3-2. Quantitation limits (QL) for grab samples and for POCIS-derived concentrations for the Comp B flume, the Comp. B positive control, and the Vieques field validation studies. Also shown are the volumes of water cleared of MC estimated using flow-corrected sampling rates (Rs).

MC	QL-grab (ng/L)*	QL-POCIS (ng/L)	Estimated vol. cleared (L)**	Vol. adjusted QL-grab (ng/L)***
Comp. B flume expt.				
TNT	21	5	11	2
RDX	46	8	15	5
Comp. B positive control study				
TNT	50	6	4	5
RDX	120	5	11	12
Vieques field validation (T14)				
TNT	25	11	12	3
RDX	54	9	24	5

*for 1-L sample

**by 3 POCIS

***adjusted for 10 L

2. For the Comp. B positive control study, the concentrations of TNT and RDX in grab samples taken at three different time points adjacent to the source were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 12 out of 20 stations, including those more distant from the source than the point of grab water sampling (Table 3-3). 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 (Table 3-3).

3. For the Comp. B positive control study, the concentrations of TNT and RDX in grab samples taken at three different time points adjacent to the source were reported as non-detects (detection frequency = 0); contrastingly, POCIS-derived TWA concentrations were reported for 12 out of 20 stations (detection frequency = 60%) (Table 3-3). For the Vieques field validation study, the concentrations of RDX in the initial grab samples were reported as non-detects for 3 out of 15 stations (detection frequency = 20%), while for final grab samples RDX was reported as non-detects for all stations (detection frequency = 0). Contrastingly, POCIS-derived TWA concentrations were reported for 11 out of 14 stations (detection frequency = 79%) (Table 3-3).

Table 3-3. Summary data for TNT and RDX detection for grab samples and for POCIS-derived concentrations obtained in the Comp. B positive control and the Vieques field validation studies.

MC	QL-grab (ng/L)	Grab concentrations (ng/L)	QL-POCIS (ng/L)	POCIS TWA concentrations (ng/L)
Comp. B positive control study				
TNT	50	<QL for all 3 samples	6	<QL for 8 stations, 9 to 103 for 12 stations
RDX	120	<QL for all 3 samples	5	<QL for 8 stations, 9 to 97 for 12 stations
Vieques field validation (target)				
TNT	25	<QL for 13 stations, 5984 for T14**	11	<QL for 13 stations, 5304 for T14
RDX	54	<QL for 12 stations, 24 - 51 for 3 stations ***	9	<QL for 3 stations, 5 to 13 for 11 stations

*for 1 L sample

**average for 2 samples

***only initial grabs samples resulted in detects

3.1.5 Performance Objective #5: Success Rate

3.1.5.1 Description

In this context, success rate refers to the percentage of field samples that are both recovered and provide useful data.

3.1.5.2 Data Requirements

Useful POCIS, water, sediment, and tissue data from target sampling locations.

3.1.5.3 Success Criteria

Useful data collected for at least 80% of sampling locations for POCIS.

Extent Success Criteria Were Met

All 20 and 30 POCIS sampling canisters deployed at Gulf Breeze and Vieques, respectively, were recovered in good condition, resulting in 100% recovery. One Vieques sample (T5) was compromised during laboratory preparation for analysis. The 153 POCIS samplers (51 canisters) placed in the flume for flow optimization and Comp B release rate studies were recovered at a rate of 100%. All tissue (Gulf Breeze), grab water (Gulf Breeze and Vieques), and sediment and sediment porewater (Vieques) samples were recovered and successfully analyzed, resulting in a success rate of 100%. Data were considered useful whether or not the concentrations were above or below method detection limits, 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 (Section 2.2; Appendix D) are a quantitative measure of the value of the POCIS data, showing negligible losses and post-uptake preservation of the parent compounds throughout the field effort.

3.1.6 Performance Objective #6: Quality Control and Quality Assurance

3.1.6.1 Description

Site- and/or experiment-specific sampling and analysis plans (e.g., demonstration plan) were developed, and were followed for each task to ensure quality control and quality assurance. Detailed elements associated with QA/QC are provided below.

3.1.6.2 Data Requirements

Chain of custody forms were originated upon collection of samples and followed the samples through processing at OSU. Quality control for all analytical chemistry samples were performed using the following measures. For each sampling trip, a blank passive sampler (field blank) was subjected to all phases of the field and transport experience. These samples were extracted and analyzed along with field samples to evaluate potential for contamination. Procedural blanks, spikes and spike duplicates were conducted at a frequency of 5% of samples extracted. Calibration of the GC/MS was performed prior to each run and checked every 10 samples. Precision and accuracy of all laboratory analytical data were monitored throughout the analytical process. Instrument precision and accuracy was be assured by conducting initial calibration curves ($r2 > 0.98$), and continuing calibration verification at a frequency of 10%. Calibration and maintenance of the MS was conducted prior to every analytical run including checking the accuracy of the tune and checking for leaks. Internal calibration was performed using stable isotope TNT. Quantitation limits were set at 3x the method detection limit and represent the lowest concentration that could be consistently used in calibration curves across fluctuating inlet conditions. Due to sample enrichment, quantitation limits are much lower for SPE (500x enrichment) and POCIS (up to 4000x enrichment) samples. Any data from samples that did not meet these criteria will be clearly flagged. Detailed analytical methods and quality control descriptions are listed in (Appendix E). Analytical methods were validated within the laboratory prior to acceptance of samples including calibration, laboratory blanks, and a quad study that consists of four replicate spiked samples as an initial measure of accuracy and precision.

3.1.6.3 Success Criteria

As defined in demonstration plan and data requirements above. In brief, all samples shall have proper chain of custody documentation and sample control. Blank samples shall be below quantitation limits. As a general rule, precision and accuracy must be within ± 35%. If these criteria are not met, associated data will be flagged. Continuing calibration will not exceed 20% of expected and must be within 20% of the expected value prior and post the sample run for data to be valid.

Extent Success Criteria Were Met

No analytes were present in any type of blank above the quantitation limits at either Gulf Breeze of Vieques. Extraction efficiencies of POCIS and SPE of water samples were always less than 25%. A few analytes in tissue and sediment had recoveries up to 30% lower. See Appendix E for more details. These changes were not significant within the reported data as slightly lower recovery did not influence our ability to detect analytes and no analytes were above quantitation limits in either matrix with lower than expected recoveries. Instrument quantitation limits were satisfactorily low with 48 µg/L for TNT, 16 and 11 for ADNT and 2-ADNT, 5 and 18 for 2,6-DNT and 2,4-DNT, and 34 µg/L for RDX. Values were set at 3x the method detection limit calculated based on variability found in seven replicate low level spikes using SPE extraction as a background. Due to sample enrichment, quantitation limits are much lower for SPE and POCIS samples and lower for oyster and sediment samples, despite similar instrument MDLs. For all samples, chain of custody and sampling handling was met. All calibration criteria and instrument maintenance was met for all final reported data.

3.2 QUALITATIVE PERFORMANCE OBJECTIVES

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

3.2.1.1 Description

MC water concentrations are the most relevant and useful measure with regard to exposure and risk assessment since uptake into most reef organisms will be through water exposure. Improving the ability to measure MC in water using integrative and sensitive techniques will greatly improve risk characterization and assessment ability across sites, reducing uncertainty and increasing toxicological significance.

3.2.1.2 Data Requirements

Development of both POCIS-derived and grab water data in a water body known to possess large quantities of underwater UXO.

3.2.1.3 Success Criteria

POCIS will provide data for adequately characterizing exposure risk to sensitive receptors at an UWMM site. Exposure data will be used in screening-level ecological risk assessment by comparing water column concentrations to available toxicological data.

Extent Success Criteria Were 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. For Vieques, POCIS-derived TWA concentrations and grab samples were 10 to 1,000,000 times lower than hazardous concentrations to 5% of species (HC5) generated from the most up to date and comprehensive species sensitivity distributions (SSD) (Lotufo et al., 2017).

3.2.2 Performance Objective #8: Ease of Operator Use

3.2.2.1 Description

3.2.2.2 Ease of Operator Use

3.2.2.3 Data Requirements

Feedback from field and laboratory technicians on usability of technology, sample prep and extraction, and time requirements.

3.2.2.4 Success Criteria

Reduced effort relative to water traditional discrete-sampling and analysis techniques.

Extent Success Criteria Were Met

Feedback in field by DoD contractors was very positive. 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 don't degrade over time (e.g., freeze or extract samples daily). Laboratory feedback indicated that

processing of POCIS in comparison with standard solid-phase extraction (SPE) of grab water samples was negligible.

3.2.3 Performance Objective #9: Cost-Benefit

3.2.3.1 Description

3.2.3.2 Cost-benefit

3.2.3.3 Data Requirements

Costs, data, and usefulness of data comparison for POCIS, water, sediment, and tissues.

3.2.3.4 Success Criteria

Relative value of data compared to cost of traditional measurements from water, sediment, and tissues.

Extent Success Criteria Were 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, providing more information to help with site managers' evaluation of ecological risk potential. It was noted, however, that at Vieques the POCIS and grab sampling efforts both resulted in the same conclusion of no ecological risk at the stations sampled, and that single grab samples are much less costly and present limited risk in comparison to need for divers. The need for divers was inherent at Vieques to achieve the study design for technology validation, but diver need is site-specific and specific to the objectives of the study. The cost-benefit of using POCIS over more traditional means of water sampling (e.g., grab or composite sampling) was examined using multiple examples in the Cost Analysis (Section 7).

3.2.4 Performance Objective #10: End-User Understanding and Acceptance

3.2.4.1 Description

End-user understanding and acceptance.

3.2.4.2 Data Requirements

Verbal and/or written feedback from site managers at the demonstration site, interested site managers from other sites, and/or other potential users of the technology that have interests or needs to understand MC exposure at UWMM sites.

3.2.4.3 Success Criteria

Feedback to gauge end-user understanding of the data provided, its value added to remedial investigations, and interest level in using the technology and/or recommending it for use at other UWMM sites.

Extent Success Criteria Were Met

Site managers and contractors understood the value of integrative samplers for MC, and provided considerable in kind support to successfully demonstrate the technology at Vieques. They expressed that public concerns regarding sampling at the wrong place and the wrong time could be alleviated, particularly by the results of the positive control study at Gulf Breeze. However, concerns were expressed about regulatory implementation and the fact that POCIS and grab samples provided the same conclusion with respect to no ecological risk. Although the cost of collecting a single grab sample at a site is less expensive than monitoring with POCIS for reasons described previously in this report, the cost for POCIS is much less than multiple grab or composite sampling required to produce integrative data equivalent to POCIS. Note, however, that the concerns expressed by Vieques site managers (diver costs and safety) are eliminated at sites where there are structures from which suspension of samplers can be done with relatively little cost.

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 western side of the island was used for the U.S. Naval Ammunition Support Detachment (NASD), while the eastern side was used as the Vieques Naval Training Range (VNTR). The former VNTR is located on the eastern half and the former NASD is located on the western one-third, with the communities of Isabel Segunda and Esperanza located in between.

East Vieques (former VNTR). The former VNTR, which comprises approximately 14,573 acres, provided ground warfare and amphibious training for U.S. Marine Corps (USMC), naval gunfire support training, and air-to-ground training. A conceptual site model for a wide area assessment (WAA) of underwater areas (referred to as UXO 16) depicts typical activities on the range (Figure 4-1). 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 (Figure 4-2).

On April 30, 2003, the former VNTR was transferred to the DOI to be operated and managed by the United States 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).

A total of 16 of the 18 Munitions Response Sites (MRS) on Vieques have been ranked a Priority 2 hazard under DoD's MRS Prioritization Protocol (MSRPP), which ranks explosive safety and environmental risk at MRSs using multiple hazard evaluation models (CH2M Hill, 2013). A Priority 2 hazard is the highest priority rating that can be scored for sites not containing chemical warfare materials. UXO 16 encompasses the underwater areas, including Bahia Salina del Sur (Figure 4-2).

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; Navy EOD, 2010), and is the focus for this technology demonstration.

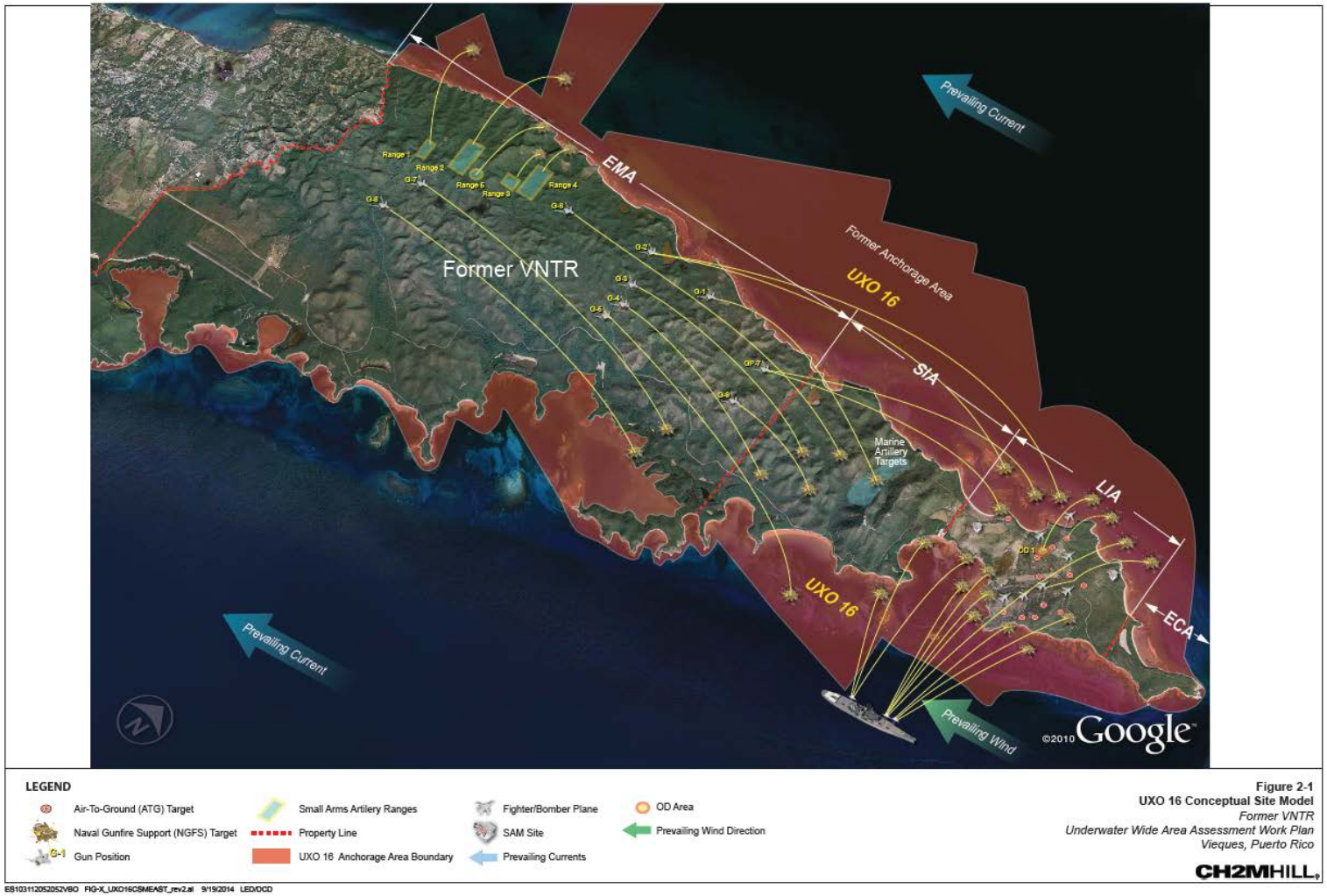

Figure 4-1. Conceptual site model (CSM) including history, physical characteristics, land use, and potential receptors at UXO 16, which includes the demonstration site, Bahia Salina del Sur. From CH2M Hill (2014).

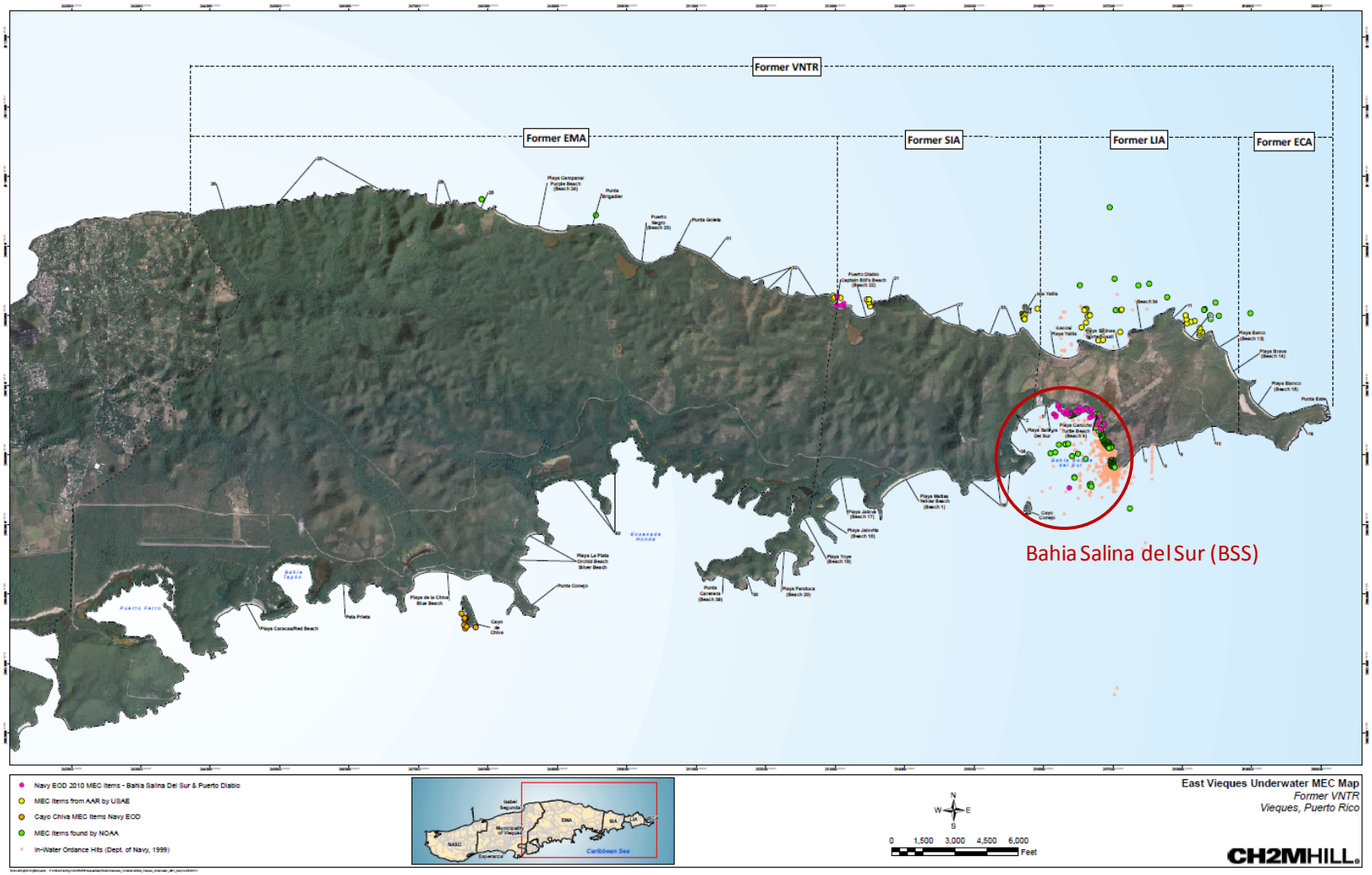

Figure 4-2. The former Vieques Naval Training Range (VNTR) on the east side of the island, showing the four operational areas and UWMM from several recent surveys in Bahia Salina del Sur.

4.2 SITE GEOLOGY/HYDROLOGY

The area of BSS is approximately 0.75 by 0.50 nautical miles with water depths up to slightly more than 30 feet (NOAA, 2010; NOAA and Ridolfi Inc, 2009; Figure 4-3 and Figure 4-4). 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, Nawojchik, and Evans, 2002) or piles of dead coral rubble (likely created by earlier ordnance detonations). The entire island of Vieques had 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).

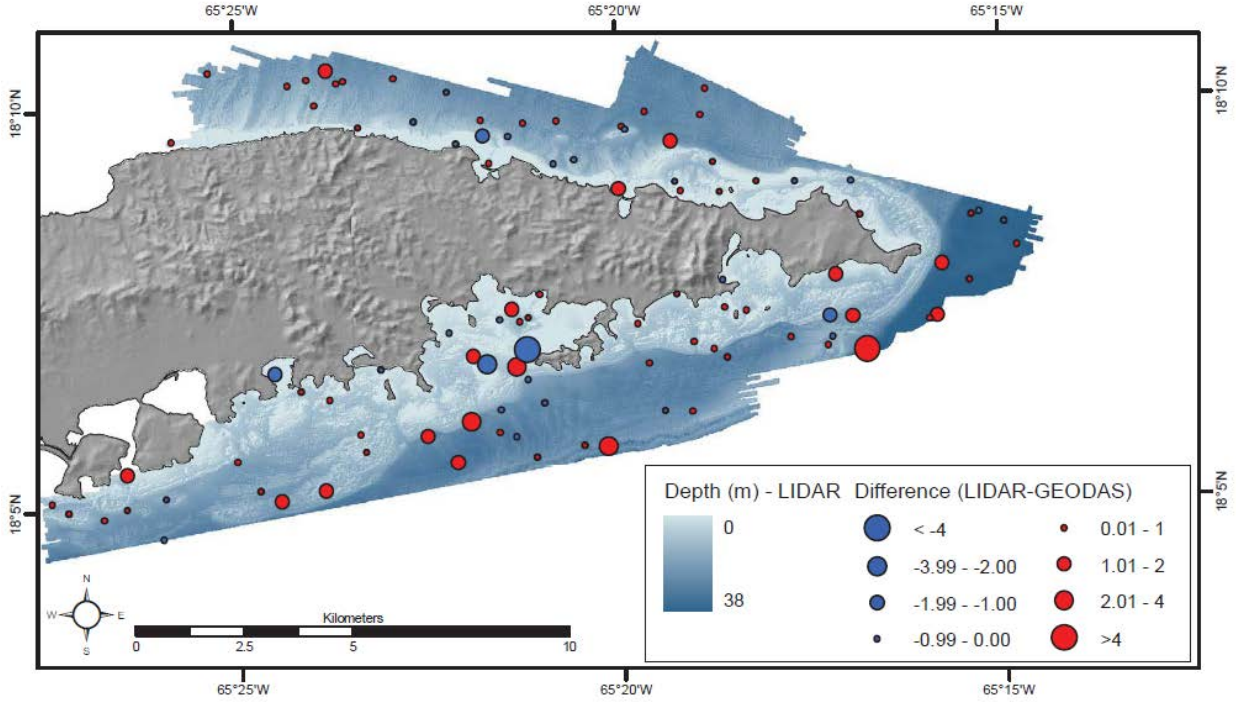

Figure 4-3. Bathymetry map around east Vieques generated from LIDAR data. The locations of 100 random points are displayed. The bubbles correspond to the difference in predicted depth values at that location. From NOAA (2010).

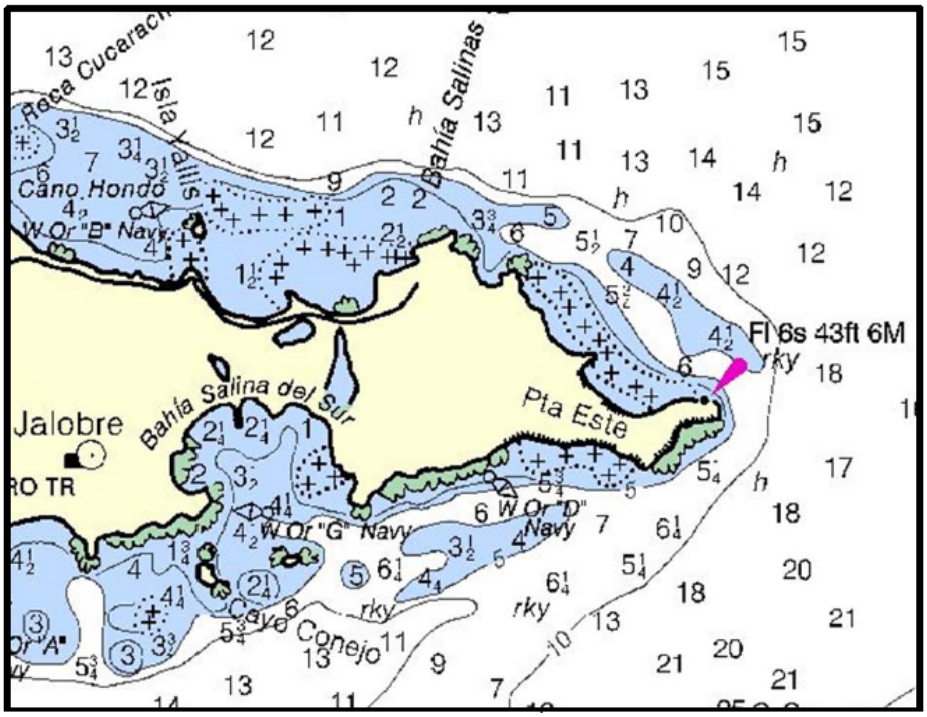

Figure 4-4. Cropped portion of NOAA chart 25650 (34th edition, April 2004, soundings in fathoms) depicting hydrography in project areas. Note: + symbols on nautical charts indicate coral outcroppings or rocks, not UXO. From NOAA and Ridolfi Inc (2009).

The vast majority of the sea bottom in BSS is sand, with less than 10% coral cover, but significant seagrass can be present ranging from patchy (10–90%) to continuous (90–100%) in some areas (NOAA and Ridolfi Inc, 2010; Figure 4-5) A series of transects out from the shoreline in 2006 revealed generally soft bottom supporting submerged aquatic vegetation in the northern portions of the bay, while the shoreline on the east side was a mixture of rubble, rocks, hard bottom and sand pockets (GMI, 2007).

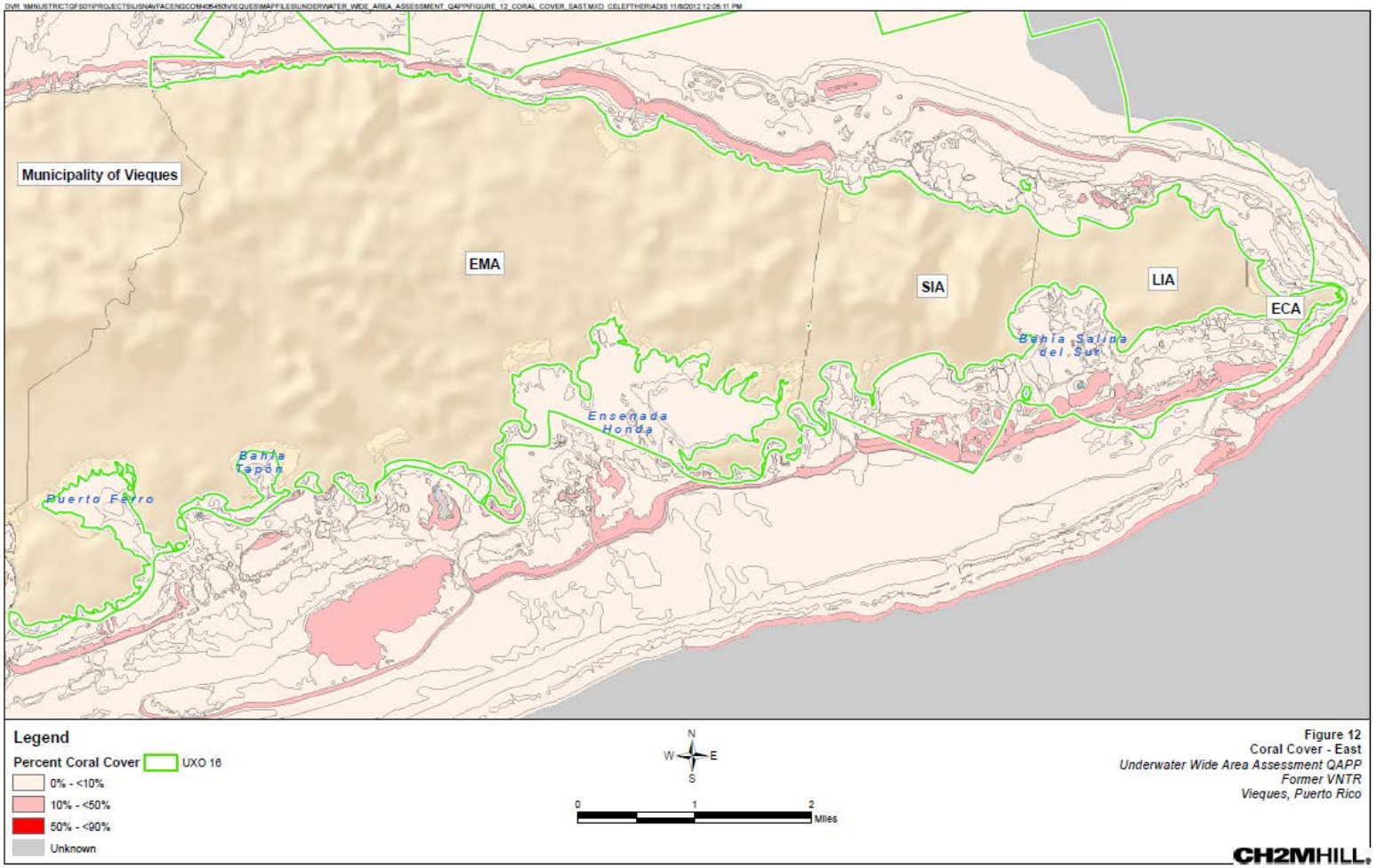

Figure 4-5. Map of the former VNTR showing percent coral cover in the underwater UXO areas. Bahia Salina del Sur was classified as primarily 0 <10% coral cover. From CH2M Hill (2014).

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/NE to west/SW 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 of 10–20 cm/s in the region with a mean vector velocity of 5 cm/s (Capella et al., 2003), but may be stronger (> 50 cm/s) in the Vieques Passage and off of the eastern end of the island (GMI, 2003). Tidal height is estimated in Vieques at 30–40 cm above and below mean low water (MLW) (Capella et al., 2003). In addition, a greater Caribbean drifter study indicated the presence of an eastward current of > 30 cm/s along the southwest coast of Vieques, continuing across the Vieques Passage towards mainland Puerto Rico (Richardson, 2005).

4.3 CONTAMINANT DISTRIBUTION

Few data were available to sufficiently characterize the extent and magnitude of MC concentrations in sediment or water at Vieques. A 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). Note, however, that the NOAA study did not perform targeted sampling immediately adjacent to breached munitions, but rather employed a stratified random design to select study sites around the island. 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/g HMX in fiddler crab (*Uca sp.*) tissues taken in the former LIA. Porter, Barton, and Torres (2011) reported various MC in water, sediment, and biota sampled at BSS, most of them taken adjacent to an unexploded, breached 2,000 pound bomb near the ex-USS KILLEN stern, representing the only underwater detection of MC at Vieques reported to date.

The paucity of data associated with the MC at BSS is expected based on the localized and unpredictable nature of release from encapsulated material in UWMM, but it is also anticipated that the POCIS technology demonstration will help resolve this uncertainty, considering the integrative nature of the sampling and low detection limits it affords.

A summary of other persistent COCs including metals, PAHs, PCBs, and organochlorine pesticides were provided concurrently with the data for energetics (Pait et al., 2010), but were below any regulatory action levels for BSS, and are outside the scope of this technology demonstration.

The documented presence of underwater UXO at BSS was one of the primary reasons for selection of this site for demonstrating the POCIS technology. Although historical reports on MC contamination in sediments, biota, or water are scarce, UWMM are potential sources of MC, and were therefore, the focus of this demonstration at Bahia Salina del Sur. The most comprehensive evidence available to us at the time of writing the project demonstration plan included that from (1) a near-shore survey focused adjacent to military targets T1 through T6 (GMI, 2007,Figure 4-6), (2) a NOAA survey with GMI ground-truthing in the central part of BSS (GMI, 2007; Figure 4-7), (3) a U.S. Navy survey primarily along the northern shoreline (Navy EOD, 2010; Figure 4-7; pink circles), and (4) coordinates from historical collection of U.S. Navy water hits from over 10 years of observations from gun fire along the south east coastline of BSS. An example of densities of verified munitions by type is shown in Table 4-1, which summarizes items found by Geo-Marine, Inc. (GMI) in the near-shore survey.

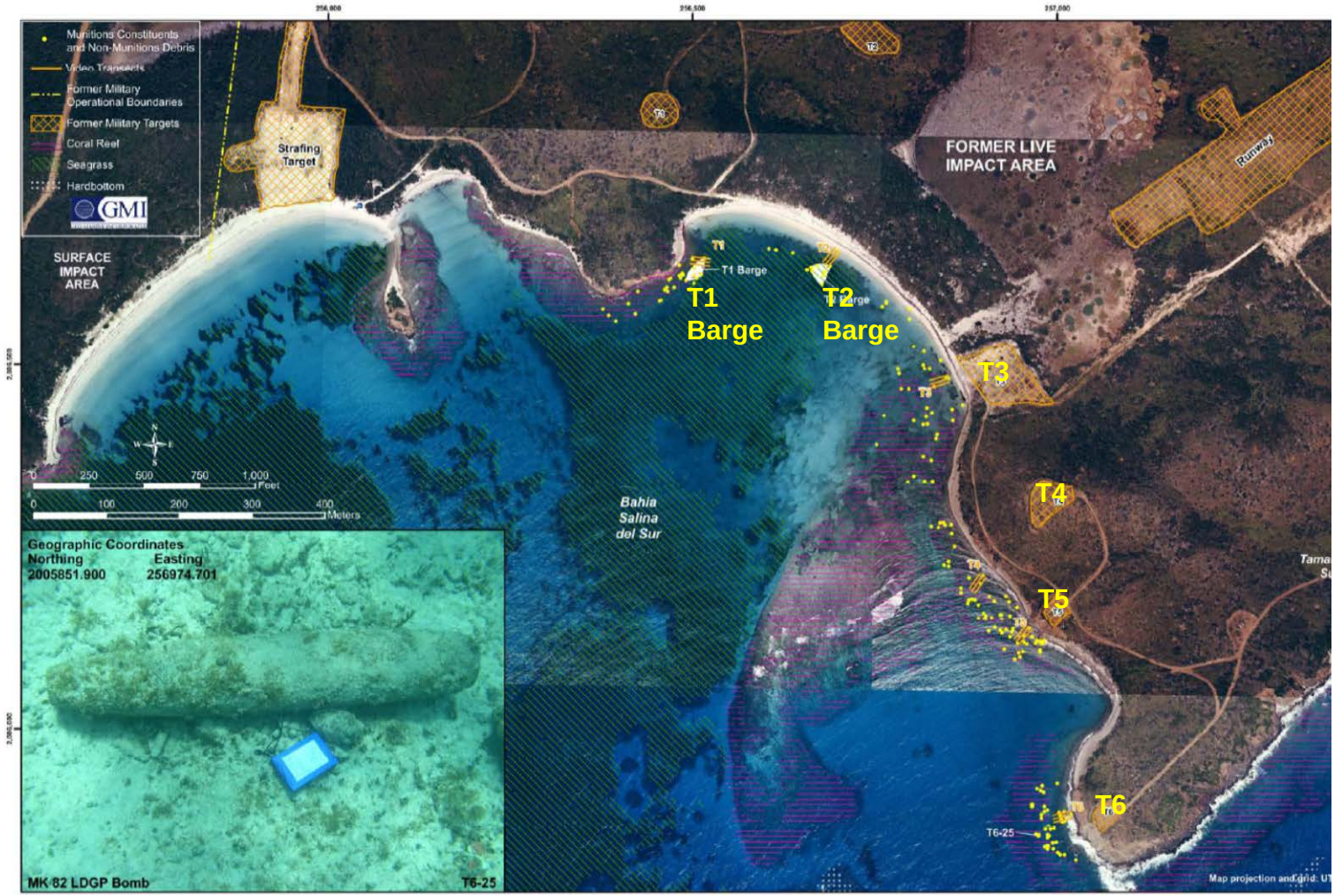

Figure 4-6. Location of munitions related items and non-munitions debris observed off former military targets T1 through T6 in the near-shore environment at Bahia Salina del Sur, Vieques. Modified from GMI (2007).

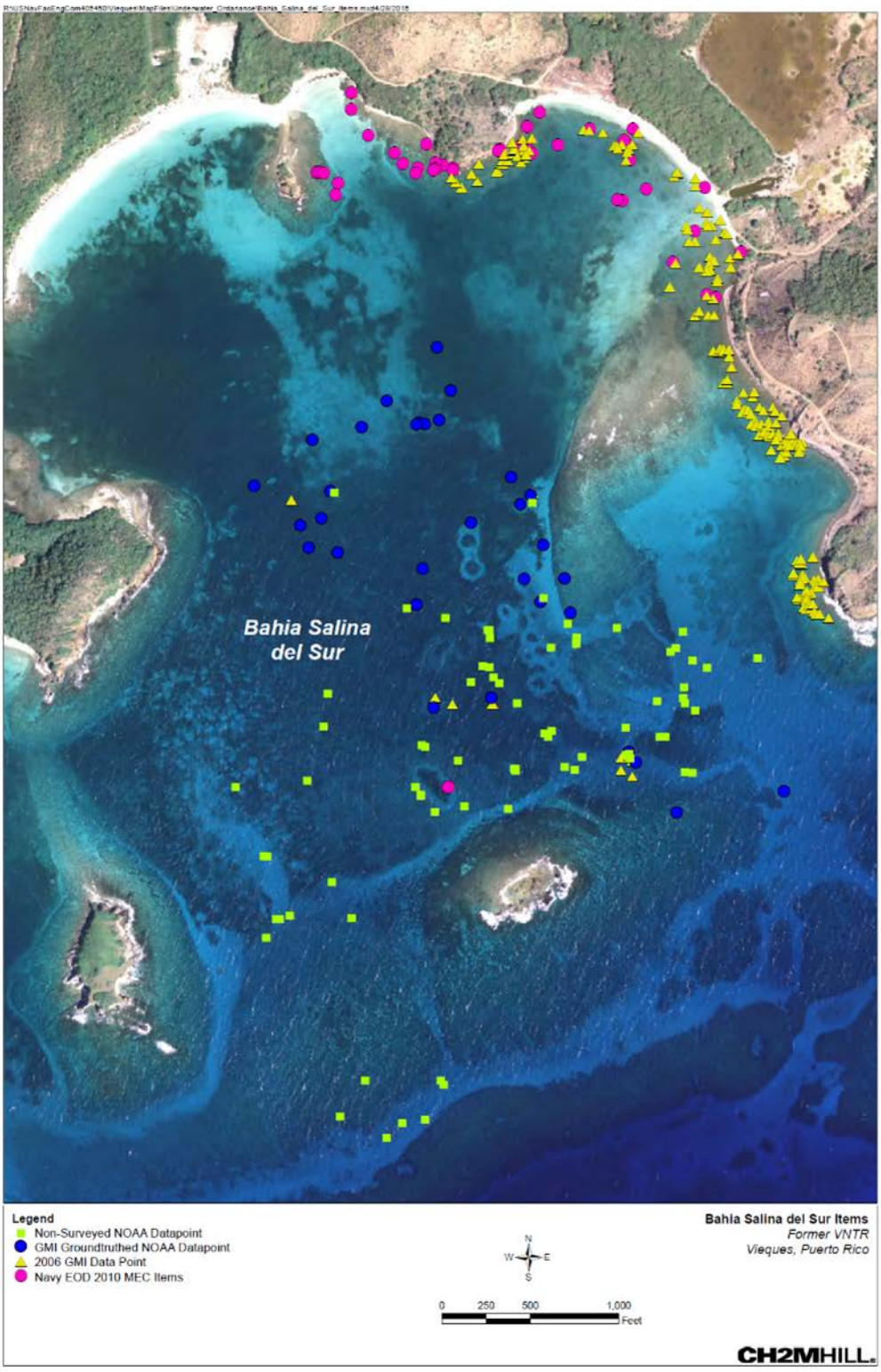

Figure 4-7. Verified munitions (e.g., not munitions debris) in Bahia Salina del Sur (BSS) from previous surveys by NOAA, 2010, GMI, 2010 and Navy EOD, 2010. From Brett Doer, CH2M Hill.

Table 4-1. Summary of type and quantity of munitions, munitions debris, and non-munitions debris found in the nearshore area off former military targets (T1 through T6) at Bahia Salina del Sur, Vieques. From GMI (2007). Targets correspond with those shown in Figure 4-6.

Munitions	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	**Total**
3 in Projectile				1		1	**2**
5 in/54 Projectile	10			24	13	34	**82**
500 lb Old Style General Purpose Bomb				1			**1**
Bomb Dummy Unit 33 Practice Bomb	1				7	2	**10**
British MK 7				1			**1**
MK 82 LDGP Bomb	12	3	2	4	2	1	**24**
MK 83 Bomb					1		**1**
Tube from inside of a 5 in Puff Round						1	**1**
Snake Eye Fins (bomb possibly attached)		1	2	2			**5**
Cylindrical Object (partially buried mine or bomb)				1			**1**
Munitions Debris	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	
5 in/54 Projectile Debris					1		
81 mm Mortar Illumination Tail Assembly				1			**1**
Base of a 5 in/54 Projectile						1	**1**
Base plate from MK 82 LDGP Bomb	1						**1**
Nose section MK 82 LDGP Bomb	1						**1**
MK 82 LDGP Bomb (spotting charges expended)				1			**1**
Fragment						1	**1**
Metal Debris			2	1			
Rockeye Half Shell Submunition Canister			1	3			**3**
Snake Eye Fins		1	6	11			**18**
Non-Munitions Debris	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	
Target debris					2	2	**4**
Tank track				2			**2**
Expended MK 24 Flare Canister		1					**1**
Metal debris		2	2	5			**12**
Metal mesh grate				1			**1**
Metal pipe				1			**1**
Total	**25**	**8**	**15**	**60**	**26**	**43**	**177**

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) time-weighted average 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 (Figure 4-6 and Figure 4-7, Table 4-1; GMI, 2007, NOAA, 2007). A conceptual diagram of the basic experimental design at Bahia Salina del Sur (BSS) is shown in Figure 5-1.

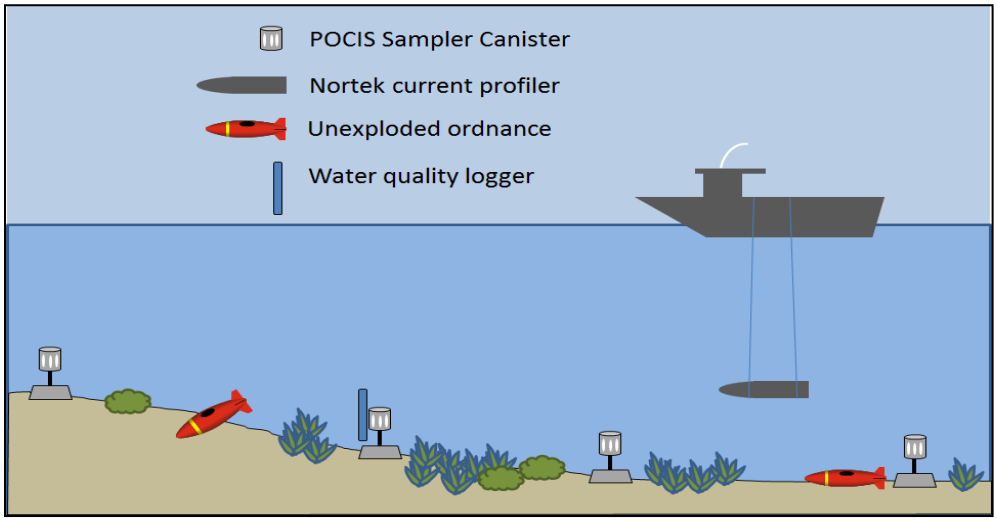

Figure 5-1. Generalized experimental approach for the technology demonstration at BSS.

The generalized experimental design at Bahia Salina del Sur (BSS) (Figure 5-2 and Figure 5-3) 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 MC. 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 an UWMM site known or suspected to contain UWMM, but with limited or even no knowledge of presence or condition of munitions. The Target 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. Note, however, that it was beyond the scope of this project to positively verify that munitions selected for the Target approach were indeed releasing MC prior to the POCIS demonstration due to the complexities associated with verification of such a scenario, and NOSSA regulations that required no direct contact with the UWMM themselves.

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 ER-2341).

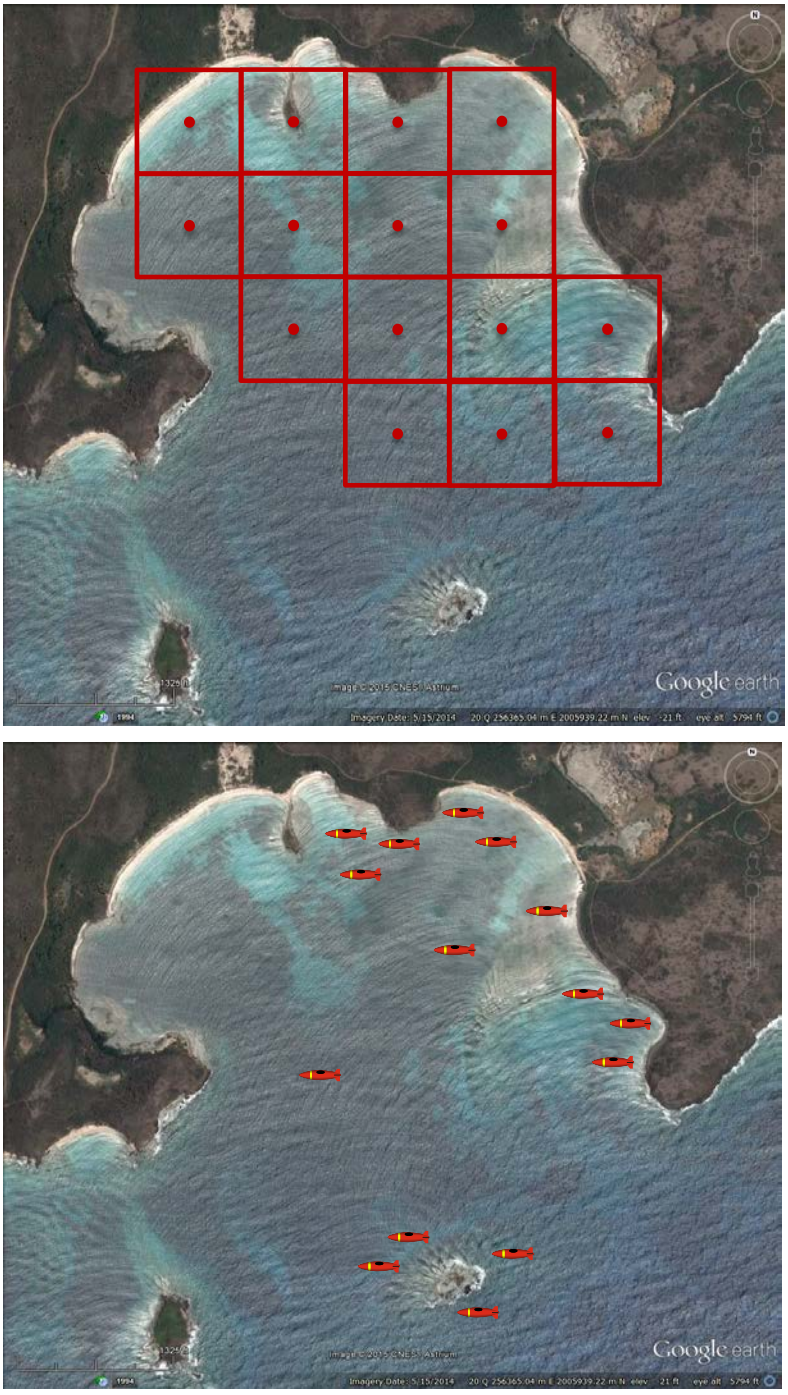

Figure 5-2. Proposed distribution of 30 POCIS sampling canisters at 15 Grid stations (top) and 15 Target stations (bottom). Actual locations identified following a Reconnaissance survey and shown in Figure 5-7.

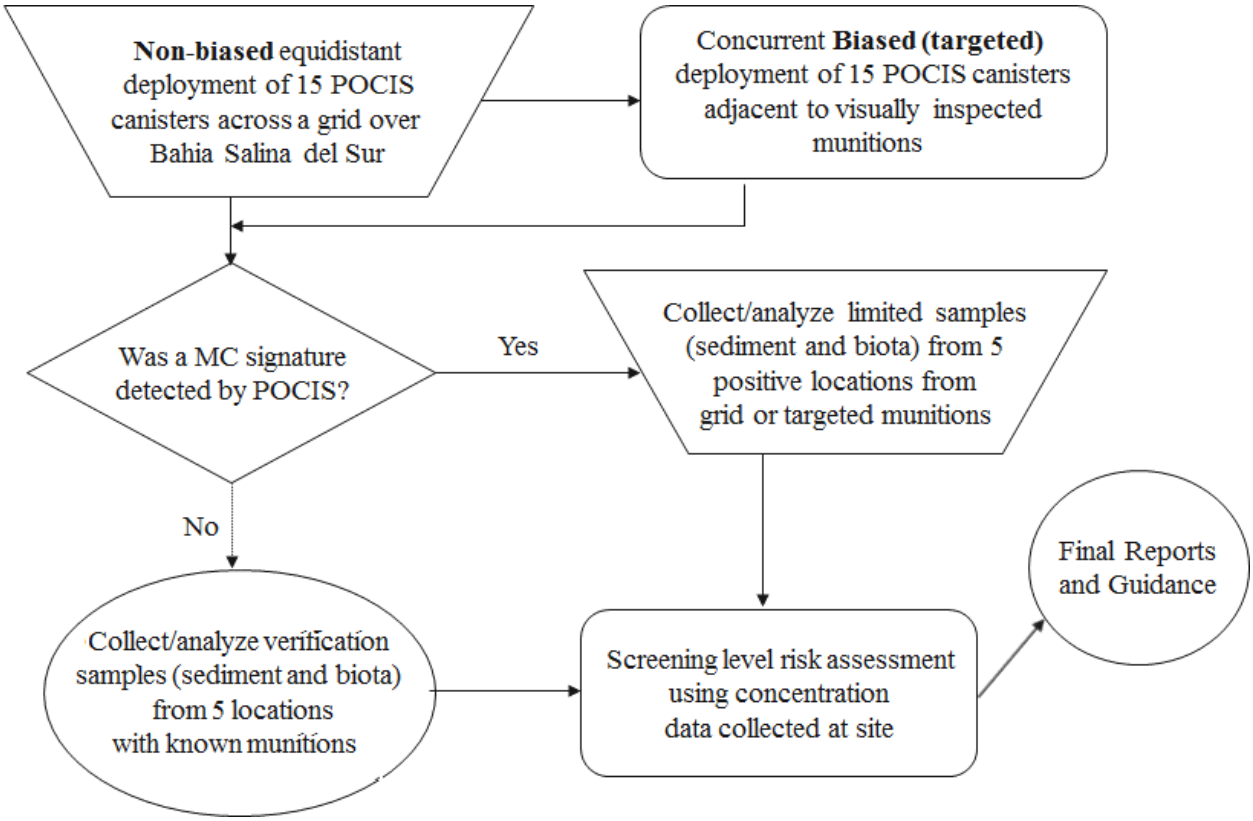

Figure 5-3. Design for POCIS demonstration at Bahia Salina del Sur, including non-biased (Grid) and biased (Targeted) sampler deployment followed by focused sampling and screening level risk assessment.

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 (NOAA, 2007, GMI, 2007; see Section 4), and critical visual inspection of candidate munitions immediately prior to this POCIS technology demonstration. Under oversight of NAVFAC LANT, 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 ETSCP project team selected 15 of these, based on detailed discussion with the MR dive team, for the POCIS deployment.

5.3 LABORATORY STUDY RESULTS

As briefly described in Section 2.2, in addition to the positive control field study in Santa Rosa Sound, FL, a series of flume experiments were conducted by the project team to optimize the calculation of R_s 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. A summary of the results from the flume studies are provided in Section 2.2.2 and full descriptions are provided in Appendices C and D.

5.4 DESIGNS AND LAYOUT OF TECHNOLOGY COMPONENTS

5.4.1 Equipment Storage and Transfers to and from the Site

Equipment was shipped to, and stored securely at the Navy Field Office at Camp Garcia located near the Department of the Interior's (DOI) entrance to the FVNTR. The office also served as a meeting location for safety and project briefs, point of origin for day trips to the field site, sample processing, and as a FedEx® pick-up location.

There are two primary means of transport to the field site at BSS: (1) by vehicle through semi-rough terrain, or (2) by boat from launch sites at Esperanza, on the south side of the island or at Bahia Icacos to the north. For this project, we launched at Esperanza pier (Figure 5-4), which required a minimum of 2 hours of travel time, including transit from Camp Garcia to the boat ramp, loading, and boat transit time to BSS.

A total of 10–12 people were typically distributed over two boats, a dive boat (Figure 5-4), and a support boat. Gear included POCIS samplers and anchoring equipment (weights, blocks, line), ice chests with blue ice, a Nortek™ current profiler, water quality meters and loggers, field notebooks, and personal items.

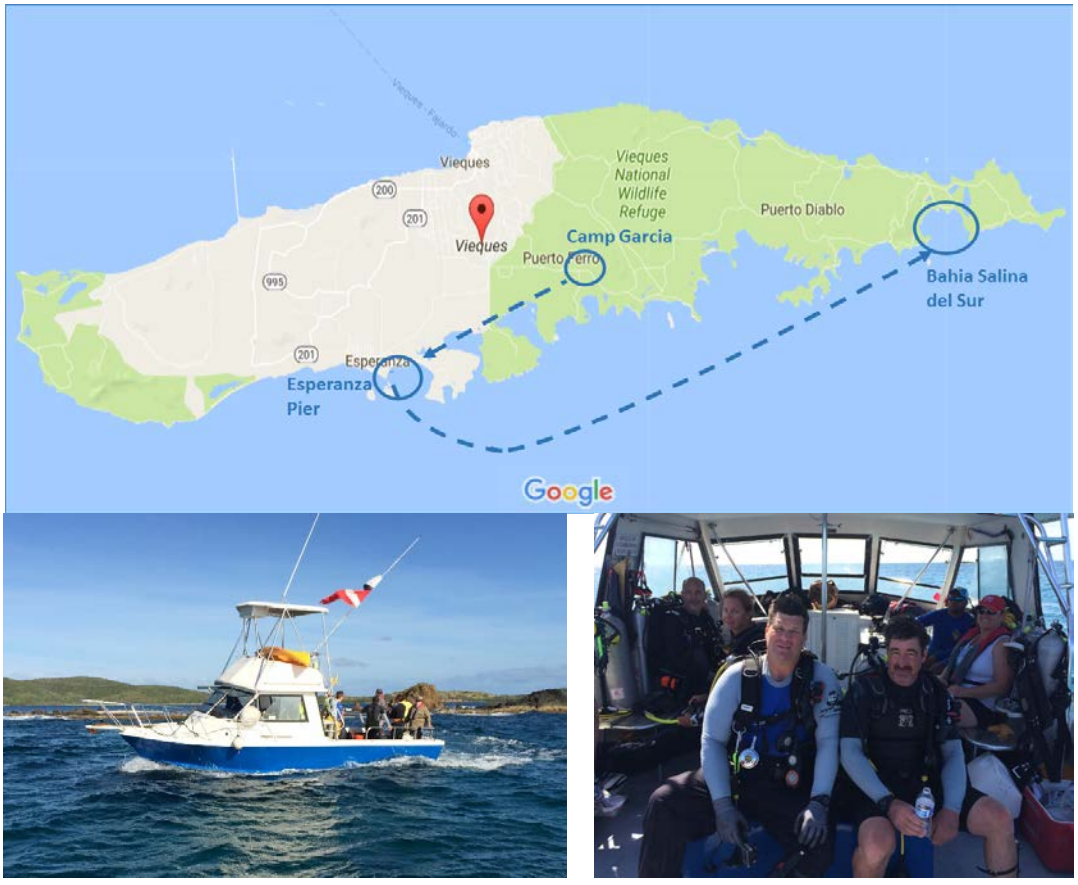

Figure 5-4. Route used to access field site from Camp Garcia (top); Vieques dive boat (bottom left) and partial crew (bottom right).

5.4.2 Listing and Description of Primary Technology Components

The small size of samplers and associated equipment with this project ensured relative simplicity of this technology demonstration (Table 5-1).

Table 5-1. List of primary technology components.

Item	Purpose
POCIS samplers	MC detection in water column, including field blanks
POCIS canisters	Protection of samplers at sampling locations
Nortek™ Current Profiler	Logging of current direction and velocity at select sampling locations
Troll® 9500 (In Situ, Inc.)	Logging of water quality (temperature, pH, salinity, dissolved oxygen) at select sampling stations
Anchoring system (36" sand screws, weights, concrete blocks, zip ties, lines, etc.)	Securing samplers and water quality sensors 12" above sea floor
Lift bags	For safe transfer and placement of POCIS at Target stations
Hand-held GPS	Documentation of placement of sampling equipment
Portable water quality meters	Documentation of water quality parameters at specified time points
Underwater still camera	Documentation of sampling locations
Underwater video camera	Real-time communication between divers and technical field crew on survey boat; video documentation at select stations.
1-L amber glass sampling jars	Discrete sampling of water and sediment
PushPoint samplers and syringe system	Collection of porewater at select locations
Sediment core liners and caps	Collection of surface sediment at select locations

POCIS canisters (each containing three samplers) were positioned approximately 12" above the sea floor. Target (i.e., adjacent to munitions) stations used a weighted-block system (Figure 5-5) weighing approximately 45 lbs. 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" sand screws were used to securely anchor POCIS canisters used at these stations (Figure 5-5). The deployment approach was fully vetted by Navy EOD, NOSSA, NOAA, and National Marine Fisheries Services based on both safety and ecological considerations. All deployed equipment was removed during the recovery operation.

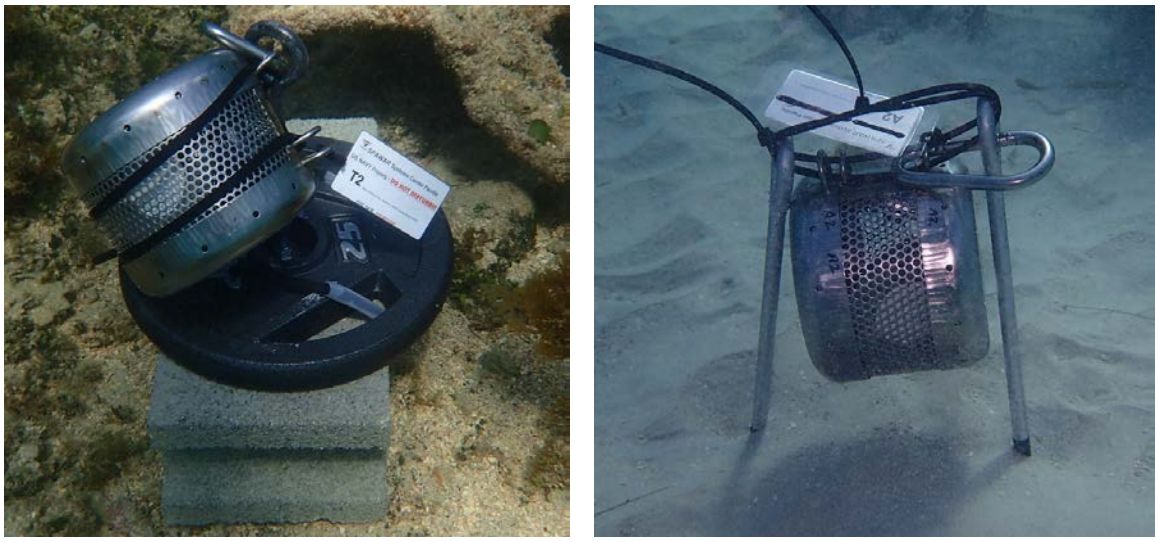

Figure 5-5. Weighted-block system (left) used for placement of POCIS adjacent to targeted munitions and sand screws (right) used to place sampling canister at Grid stations.

5.5 FIELD TESTING

Mobilization and demobilization requirements for the demonstration were minimized to the extent possible, with relevant components being conducted by project team collaborators at their respective laboratories prior to, or following, on-site field activities. 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 munitions response diver procedures) while on site.

In brief, the demonstration included: (1) site-specific anchoring trial, (2) reconnaissance study to select candidate munitions, (3) technology component deployment (3 field days), (4) technology component recovery (3 field days), followed by (5) a one-time focused verification sampling effort of porewater and sediment (2 field days) based on results from phases 1 and 2. The schedule for the technology demonstration is summarized in Table 5-2.

Table 5-2. Overview of on-site activities to support technology demonstration at Bahia Salina del Sur, Vieques.

Event	Date(s)	Tasking
Anchoring Trial	Dec 8–10, 2015	• Deployed POCIS at three stations at BSS using different anchoring options to assess anchor performance • Water surface reconnaissance study
Equipment Shipment	Dec 1–30, 2015	• Supply/equipment purchasing followed by shipment to Camp Garcia office
Reconnaissance Survey	Jan 6–9, 2016	• MR and scientific divers identify and rank 25 candidate munitions for technology demonstration • Technical team evaluation and final decision on munitions targeted for sampling
Deployment	Jan 9–16, 2016	• Field team logistical/safety briefs • Preparation of anchoring systems • Loaded POCIS canisters, calibrate instrumentation • Deploy samplers (3-day field effort) • Concurrent collection of current and water quality data • Time Initial grab sampling, on-site extraction, shipment • Field team debrief
Recovery	Jan 30–Feb 4, 2016	• Field team logistical/safety briefs • Recover samplers (3-day field effort) • Concurrent collection of current and water quality data • Time Final grab sampling, on-site extraction • Shipment of all samplers and equipment to labs • Field team debrief
Sediment sampling prep	June 1–30, 2016	• Field trials for in situ porewater sampling in San Diego • Procurement and shipment of sediment sampling gear
Sediment Sampling	July 11–14, 2016	• Field team logistical/safety briefs • Porewater and sediment sampling (2-day field effort) • On-site extraction of porewater samples • Shipment of sediments and porewater to labs • Field team debrief

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 approximate total area of the grid is ~ 10^6 m^2 (~ 250 acres), with individual sampling canisters approximately 250 m apart. Samplers were placed as close to previously derived GPS coordinates as possible, but were never placed on top of coral colonies or any ecologically important species or habitat, per on-site review by munitions and scientific divers, and specialized observers (e.g., Ms. Diane Wehner, NOAA). Due to the relatively large size of each sampling box within the grid, there were no issues associated with locating appropriate anchoring locations, based on the generally soft bottom nature of most of the site (Bauer et al., 2010). While the Grid stations were deployed using installation of 36” 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 5-6).

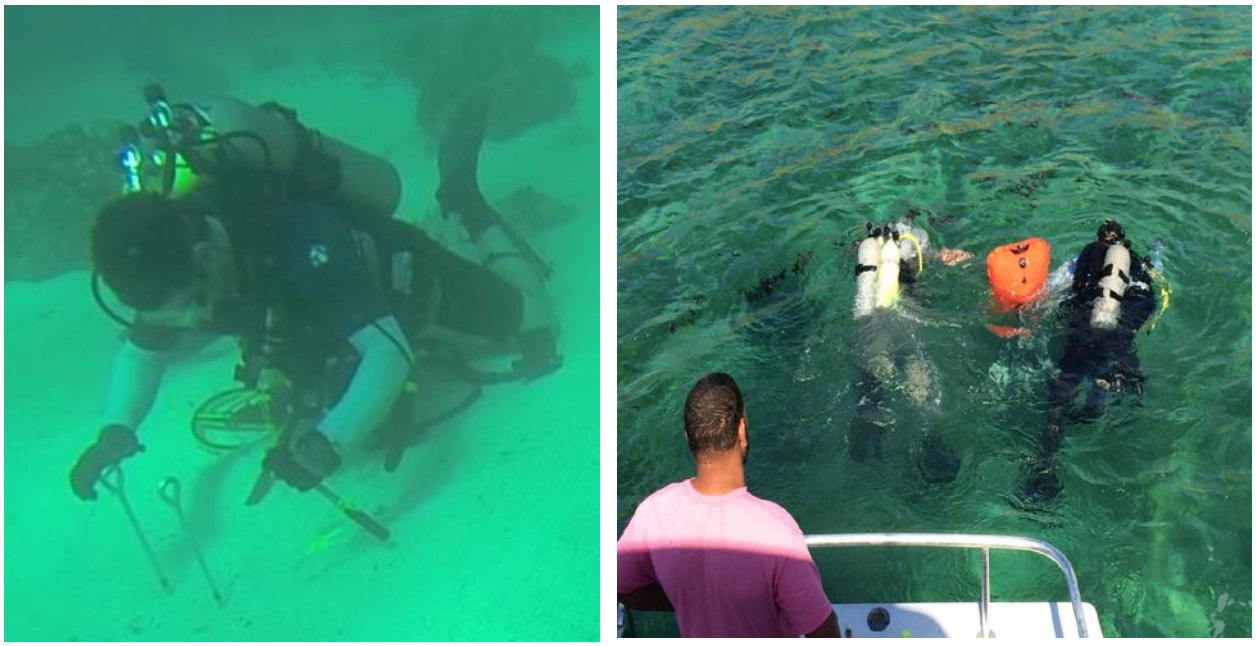

Figure 5-6. Sand screws were used to secure Grid stations to sea floor after clearance with a magnetometer (left). Lift bags were used to transport the weighted block system used to position POCIS canisters within 12" of Target munitions (right).

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 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.

Figure 5-7 and Table 5-3 show actual locations where Grid and Target samplers were deployed. Table 5-3 provide descriptors of the munition type, condition, depth, and/or substrate at each sampling location.

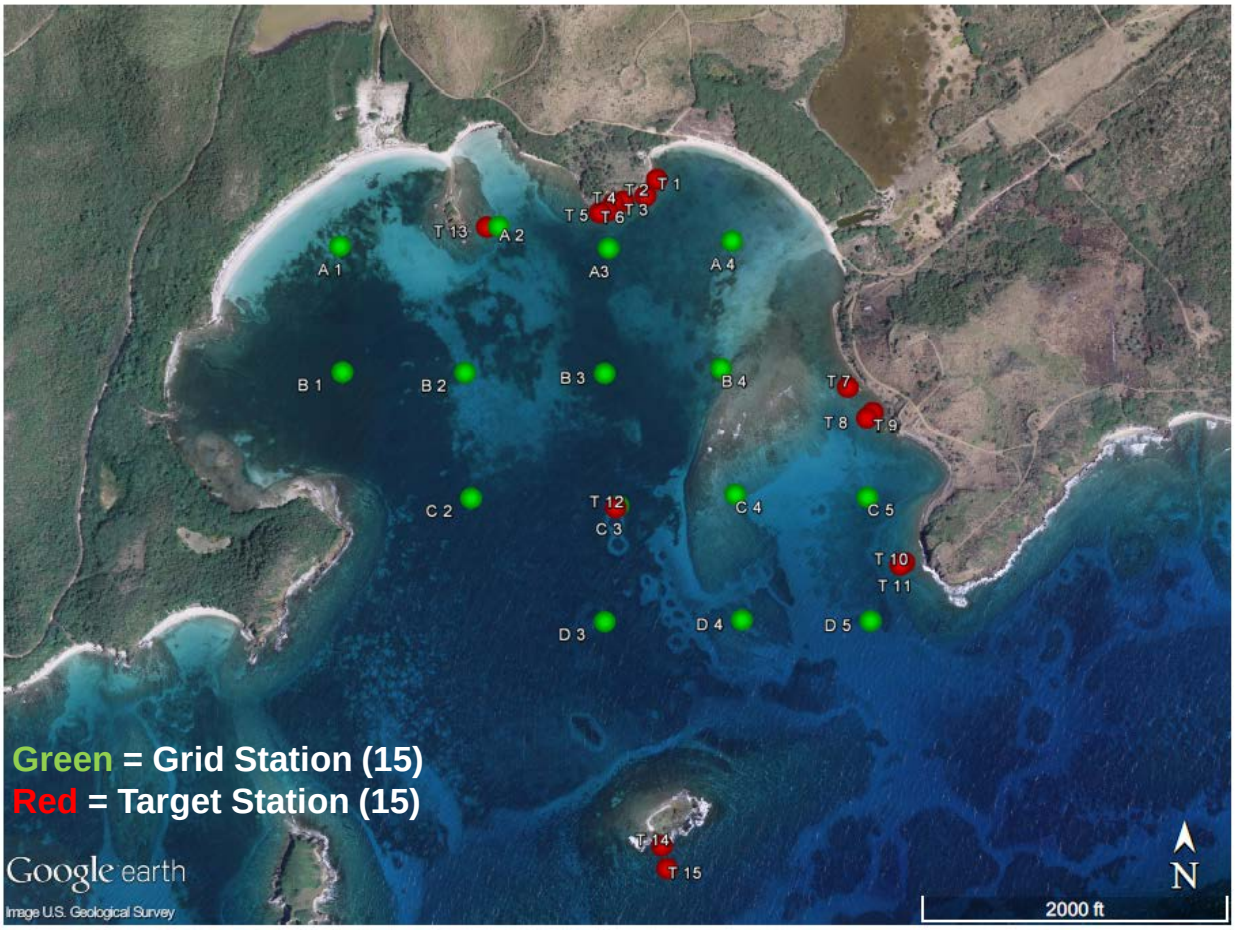

Figure 5-7. Deployment locations of Grid and Target POCIS deployments.

Table 5-3. Locations and times of deployment and recovery of POCIS at Bahia Salina del Sur. OWB=Open water blank.

Station ID	Target or Grid Station	Latitude	Longitude	Northing	Easting	Date/Time on Station	Time of UXO Clearance	Time of POCIS Deployment	Date/Time of POCIS Recovery	Deployment Duration (days)
T1	Target	18.1349890	-65.3013780	2006643	256503	1/12/2016 10:24	1/12/2016 10:24	1/12/2016 10:30	2/1/2016 12:18	20.1
T2	Target	18.1346970	-65.3015940	2006611	256480	1/12/2016 10:36	1/12/2016 10:38	1/12/2016 10:38	2/1/2016 11:53	20.1
T3	Target	18.1346020	-65.3020060	2006601	256436	1/12/2016 10:45	1/12/2016 10:50	1/12/2016 10:50	2/1/2016 11:56	20.0
T4	Target	18.1345470	-65.3022030	2006595	256415	1/12/2016 10:55	1/12/2016 11:00	1/12/2016 11:00	2/1/2016 12:03	20.0
T5	Target	18.1344180	-65.3023150	2006581	256403	1/12/2016 11:11	1/12/2016 11:11	1/12/2016 11:12	2/1/2016 12:07	20.0
T6	Target	18.1343621	-65.3024563	2006577	256388	1/12/2016 11:20	1/12/2016 11:21	1/12/2016 11:21	2/1/2016 12:10	20.0
T7	Target	18.1312020	-65.2977860	2006219	256878	1/12/2016 14:00	1/12/2016 13:55	1/12/2016 14:00	2/1/2016 14:52	20.0
T8	Target	18.1306290	-65.2974310	2006155	256915	1/12/2016 14:05	1/12/2016 14:15	1/12/2016 14:15	2/1/2016 14:40	20.0
T9	Target	18.1307290	-65.2973260	2006166	256926	1/12/2016 14:20	1/12/2016 14:25	1/12/2016 14:25	2/1/2016 14:49	20.0
T10	Target	18.1279480	-65.2968080	2005857	256977	1/12/2016 14:20	1/12/2016 14:30	1/12/2016 14:30	2/2/2016 13:00	20.9
T11	Target	18.1279990	-65.2967240	2005863	256986	1/12/2016 14:36	1/12/2016 14:37	1/12/2016 14:37	2/2/2016 13:06	20.9
T12	Target	18.1290000	-65.3021590	2005981	256412	1/13/2016 12:25	1/13/2016 12:35	1/13/2016 12:35	2/2/2016 12:50	20.0
T13	Target	18.1341200	-65.3045880	2006551	256162	1/13/2016 14:40	1/13/2016 15:00	1/13/2016 15:10	2/1/2016 15:25	19.0
T14	Target	18.1228200	65.3013000	2005295	256495	1/14/2016 9:17	1/14/2016 9:35	1/14/2016 9:56	2/2/2016 10:30	19.0
T15	Target	18.1224000	65.3011900	2005249	256505	1/14/2016 9:17	1/14/2016 9:35	1/14/2016 10:10	2/2/2016 10:46	19.0
A1	Grid	18.1337721	-65.3073521	2006516	255869	1/13/2016 13:52	1/13/2016 13:58	1/14/2016 14:02	2/3/2016 10:00	19.8
A2	Grid	18.1337415	-65.3048979	2006552	256186	1/13/2016 14:40	1/13/2016 15:00	1/13/2016 15:20	2/1/2016 14:00	18.9
A3	Grid	18.1337310	-65.3022970	2006505	256404	1/11/2016 15:13	1/11/2016 15:24	1/11/2016 15:35	2/3/2016 9:47	22.8
A4	Grid	18.1338690	-65.2999720	2006517	256650	1/11/2016 14:32	1/11/2016 14:42	1/11/2016 14:56	2/3/2016 9:38	22.8
B1	Grid	18.1314680	-65.3073020	2006261	255871	1/11/2016 11:19	1/11/2016 11:21	1/11/2016 11:36	2/3/2016 10:13	22.9
B2	Grid	18.1314590	-65.3049970	2006257	256115	1/11/2016 11:56	1/11/2016 12:07	1/11/2016 12:17	2/3/2016 10:22	22.9
B3	Grid	18.1314450	-65.3023710	2006252	256393	1/11/2016 12:49	1/11/2016 12:55	1/11/2016 13:15	2/3/2016 10:34	22.9
B4	Grid	18.1315350	-65.3001800	2006259	256625	1/11/2016 13:33	1/11/2016 13:44	1/11/2016 13:58	2/3/2016 10:43	22.9
C2	Grid	18.1291689	-65.3048817	2006003	256124	1/13/2016 13:05	1/13/2016 13:14	1/13/2016 13:27	2/2/2016 14:45	20.1
C3	Grid	18.1290280	-65.3021120	2005984	256417	1/13/2016 12:25	1/13/2016 12:35	1/13/2016 12:46	2/2/2016 12:22	20.0
C4	Grid	18.1292350	-65.2999140	2006004	256650	1/13/2016 11:39	1/13/2016 11:47	1/13/2016 12:00	2/2/2016 15:00	20.1
C5	Grid	18.1291842	-65.2974223	2005995	256913	1/13/2015 11:02	1/13/2016 11:08	1/13/2016 11:20	2/3/2016 9:19	20.9
D3	Grid	18.1269133	-65.3023630	2005750	256387	1/14/2016 11:02	1/14/2016 11:15	1/14/2016 11:28	2/2/2016 14:08	19.1
D4	Grid	18.1269420	-65.2997890	2005750	256660	1/14/2016 11:43	1/14/2016 11:49	1/14/2016 11:49	2/2/2016 13:53	19.1
D5	Grid	18.1269302	-65.2973640	2005746	256917	1/14/2016 12:11	1/14/2016 12:28	1/14/2016 12:37	2/2/2016 13:38	19.0
OWB		18.1259	-65.31028	2005649	255548	1/12/2016	-	-	-	-
OWB		18.12505	-65.31219	2005557	255345	1/12/2016	-	-	-	-
OWB		18.12447	-65.31429	2005496	255122	1/12/2016	-	-	-	-

Table 5-4. Description of munitions items, POCIS placement, and substrate/habitat at Target stations.

Station ID	Depth on Station (ft)	UXO Type	UXO Detail	Proximity of POCIS to UXO at Placement	Proximity of POCIS to UXO at Recovery	Substrate/Habitat Info in Vicinity
T1	4	MK-82	Broken Open	1.8' (21.6"), right side near base, near major crack, relative to nose on south side	Unchanged	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians; Porites sp. common at item.
T2	7	MK-82	Large Split, low order detonation, at the base.	Down current beach surge 12"	Unchanged	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians.
T3	7	MK-82 on top of one 5" round, another 5" round ~6' away. Likely HE	Nose sheared, underneath, intact, moderate corrosion	Down current beach surge 12" off the nose	Unchanged	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians.
T4	5	MK-82	Cut in half, could contain explosives, possible low order detonation	Down current 12"	0" from item (butted up to base)	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians.
T5	8	MK-82	Broken open, explosives potentially present, POCIS near the base	Down current 12"	Unchanged	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians.
T6	9	5" projectile	Broken, split down middle, no fuse visible	Down current 12"	Unchanged	Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians.
T7	4	5" projectile	fuzed, severe corrosion	Down current 12"	Now ~30"	Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians.
T8	5	500 lb General Purpose bomb	fused, moderate corrosion, no tail fin, intact	Down current beach surge, in coral, side 12"	Unchanged	Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians.
T9	6	5" projectile	intact, partial fuze remaining, corrosion	Down current 12"	Unchanged	Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians.
T10	17	MK-82, two 3" projectiles nearby	Fused, severe corrosion, no cracks	Down current 6"	Unchanged	Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians.
T11	17	16" projectile	No fuse, cut in half, visible fill material, moderate to severe corrosion, still see rotating bands	Placed at base, 6" away from broken end	Unchanged	Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians.
T12	23	MK-82	MK-82 LDGP bomb. Nose-up 1/4 proud. Edge seagrass.	Side, down current, beach surge 12"	Unchanged	Within edge of sand halo amongst scattered coral/rock; continuous seagrass (90-100%) at northern edge.
T13	?	5" projectile	Intact	Down current 12" from base	Unchanged	Colonized bedrock: Exposed bedrock contiguous with the shoreline that has coverage of macroalgae, hard coral, and gorgonians.
T14	20	1000lb General Purpose Bomb	Corrosion, visible breach(es).	Side - 12" from multiple small breaches	Unchanged	Colonized boulders and bedrock: Patchy coverage of macroalgae and gorgonians, sparse hard corals.
T15	18-19	1000lb General Purpose Bomb	Intact. Encrusted with corals, sea fans.	Down current -side 12" ~	Unchanged	Colonized Pavement: Flat, low relief, solid carbonate rock and some sand with coverage of macroalgae, hard coral, and gorgonians.

Table 5-5. Description of substrate/habitat at Grid stations.

Station ID	Depth on Station (ft)	Additional Substrate/Habitat Info in Vicinity	Sampler Intact on Recovery?
A1	12	Within edge of seagrass community (~80% cover); adjacent to large area of mostly bare sand.	Yes
A2	9	Within sand halo at edge of colonized bedrock, as characterized for station T13	Yes
A3	17	Continuous seagrass, 90-100%	Yes
A4	8	Continuous seagrass, 90-100%	Yes
B1	17	Continuous seagrass, 90-100%	Yes
B2	19	Patchy (discontinuous) Seagrass (50 percent to less than 70 percent cover)	Yes
B3	18	Continuous seagrass, 90-100%	Yes
B4	8	Continuous seagrass, 90-100%. Good surge, hard pan, difficult to deploy	Yes
C2	21	Continuous seagrass, 90-100%	Yes
C3	23	Within sand halo amongst scattered coral/rock; continuous seagrass (90-100%) immediately north.	Yes
C4	17	Within sand at eastern edge of colonized pavement: gently sloping carbonate rock with coverage of macroalgae, hard coral, and gorgonians.	Yes
C5	19	Patchy macroalgae (50-90%) and sand	Yes
D3	30	Continuous seagrass, 90-100%	Yes
D4	26	In sand patch within colonized pavement: gently sloping carbonate rock with coverage of macroalgae, hard coral, and gorgonians.	Yes
D5	33	Sand with patchy macroalgae (~10%), adjacent seagrass areas (50-70%). Hard pack bottom approximately 17" below sand	Yes

5.5.3 Discrete Water Sampling for MC

Water was sampled by two means: (1) POCIS, and (2) 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 from January 11 through 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 (Figure 5-8). Because of the propensity for some MC to rapidly degrade, grab water samples were extracted on site on to Oasis® HLB cartridges (Appendix E) and frozen before shipment to the OSU analytical laboratory.

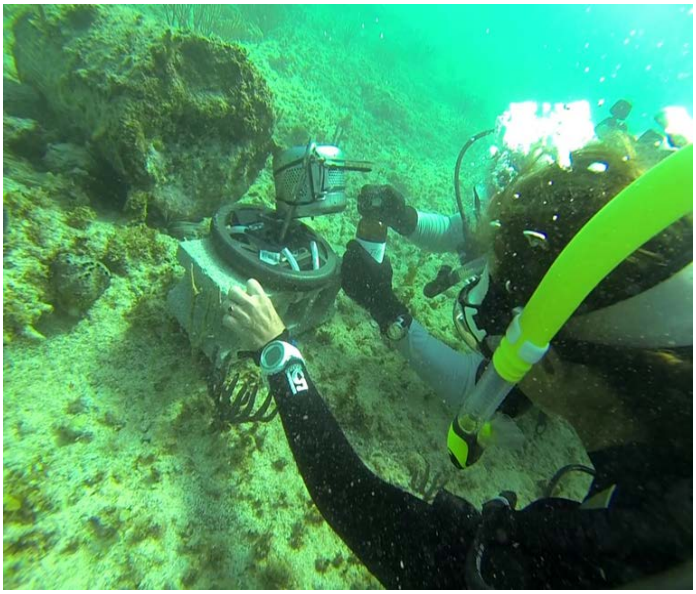

Figure 5-8. Grab sampling approach used to compare water concentrations between discrete samples and POCIS.

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. This included measurements over a total of 6 days during the 19–23 day (station-specific; average 20.5 days) POCIS exposure period. Water quality data were logged every minute, while current data were logged every 5 seconds during each deployment of the systems.

Figure 5-9. Nortek™ current profiler and Troll assembly configuration for measuring current velocity/direction and water quality adjacent to POCIS samplers. The same configuration was attached to a weighted block system at most stations for easier deployment and recovery using a lift bag.

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 5-10), essentially eliminating the need to remove surficial debris or biofouling from the samplers. POCIS were individually wrapped, frozen, and shipped overnight to Dr. Belden's lab (OSU).

Figure 5-10. 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. Weather conditions did not allow a visit to the one station where a relatively large TNT detection was observed. Earlier iterations

of the sampling plan included biota sampling, but following discussion with NAVFAC personnel and regional stakeholders, the final decision was not to collect biota samples.

The sampling design for porewater sampling is shown in Figure 5-11. Due to the desire for low detection limits, a total of 16 60-mL syringes full of porewater were collected using PushPoint samplers (http://mheproducts.com/) and composited for each sample, both at representative Inner locations (~ 0.5 m from munition) and Outer locations (1 to 2 m from munition; Figure 5-11, Figure 5-12). This approach yielded approximately 1 L of porewater from each inner and outer sampling location at the four stations: A1, T10, T11, and T12 (see Figure 5-7). As with grab samples collected during the POCIS demonstration, porewater was extracted on-site using Oasis® HLB SPE cartridges under vacuum prior to freezing and shipping. Blank BSS bay water samples and matrix spikes to bay water were extracted on-site as well.

For the sediment sampling effort, 5" 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 ESA requirements.

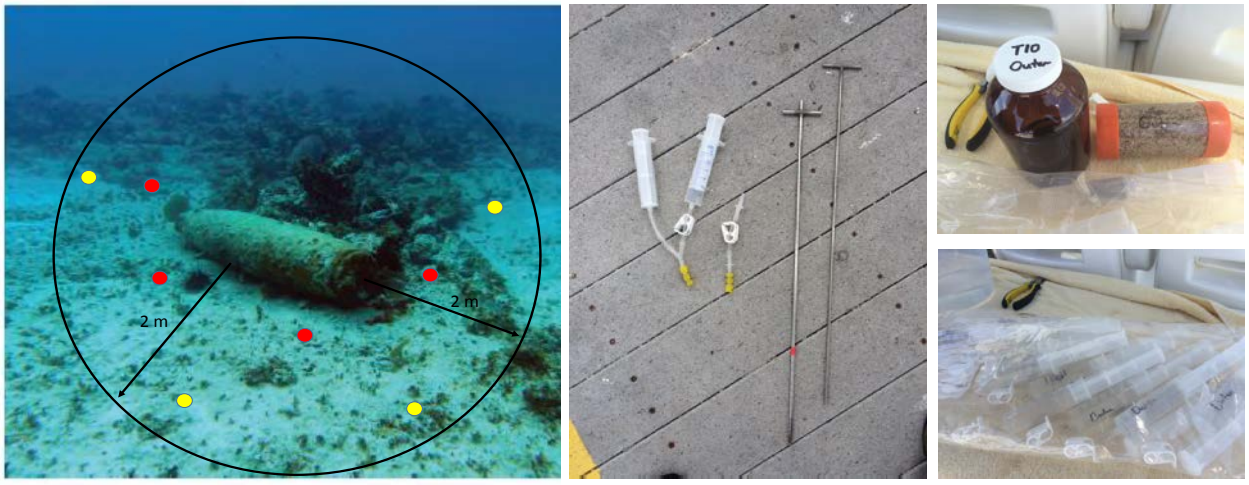

Figure 5-11. Example of porewater sampling locations ~ 0.5 m (red dots) and 1 to 2 m (yellow dots) away from a munition (left); PushPoint porewater sampler, with syringes (center); intact sediment core sample and grab water sample (top right); multiple syringes collected using PushPoint sampler from a single station for a 1-L composite (bottom right).

Figure 5-12. (left) Close-up of porewater sampling using PushPoint sampler, targeting top 6" sediment layer; (right) Inner station (~ 0.5 m from munition at Target Location T12) porewater sampling.

5.6 SAMPLING METHODS

Details associated with the sampling associated with the demonstration at BSS (Task 4) are included in Table 5-6 and Table 5-7. As the performance criteria for the technology are also measured from other associated tasks, the sampling details from those efforts (Tasks 1 and 2) are included as well.

Table 5-6. Total number and types of samples collected.

Component	Matrix	Number of Samples	Analyte(s)	Location
Task 1 Pre-demonstration sampling (Controlled Field Validation)	Water (POCIS)	66 (composited to 22)	TNT, 2ADNT, 4ADNT, DANT, RDX	19 samplers near Comp B source at EPA Dock, Pensacola, FL, 1 far-field location, 2 QA/QC.
	Water (SPE)	10	TNT, 2ADNT, 4ADNT, DANT, RDX	Grabs immediately above Comp B source canister
	Water	Varied	Flow direction and velocity with ADV	Adjacent to source canister
	Water	Continuous logging	pH, temperature, salinity	Adjacent to source canister (bottom and surface)
Task 2 Pre-demonstration sampling (Flume Calibration)	Water (POCIS)	153 (composited to 51)	TNT, 2ADNT, 4ADNT, DNT, DANT, RDX	Up to 11 locations within flume (8 exposed, 3 caged); 5 flume expts under 3 flow velocities and 2 Comp B release rates.
	Water (SPE)	63	TNT, 2ADNT, 4ADNT, DNT, DANT, RDX	12 grabs X 5 expts + QA/QC for calibrating flow-dependent Rs
	Water	Multiple discrete	Flow direction and velocity with ADV	Multiple locations and time points within flume
	Water	Continuous logging	pH, temperature, salinity	One upstream location within flume, 3 expts.
Task 4 Technology performance sampling (Vieques Island)	Water (POCIS)	90 (composited to 30)	TNT, 2ADNT, 4ADNT, DNT, RDX, picric acid	3 POCIS/canister, 15 canisters equally spaced in BSS, 15 at targeted near munitions
	Water (SPE)	33	TNT, 2ADNT, 4ADNT, DNT, RDX, picric acid	15 select locations co-located with POCIS, during deployment and recovery phases + blanks
	Water	5	DOC, TSS	Co-located with POCIS during deployment only
	Sediment	8 (composited to 4)	TNT, ADNTs, DNTs, RDX	4 locations in BSS based on positive POCIS results
	Porewater	8 (composite from 16 syringes/stn)	TNT, ADNTs, DNTs, RDX	4 locations in BSS based on positive POCIS results
	Sediment	5	TOC, grain size	4, co-located with sediment local MC stations

Table 5-7. Analytical methods for sample analysis.

Matrix	Analyte	Method	Container	Preservative[1]	Holding Time
Water (POCIS)	Munitions Constituents[2]	Solvent Elution GC/MS[3]	Aluminum foil /polyethylene Ziploc® bag	<4°C, freeze on lab arrival	28 d after frozen
Water (Grab)	Munitions Constituents[2]	SPE GC/MS[3]	1L Amber Jar	<4°C	4 d[4]
	DOC	EPA Method 415.3	0.25 L Amber Jar	<4°C, freeze on lab arrival	4 d
	TSS	EPA Method 160.2	1L HDPE	<4°C	7 d
Porewater	Munitions Constituents[2]	SPE GC/MS[3]	Plastic syringes composited into 1L Amber Jar	<4°C	4 d[4]
	DOC	EPA Method 5310C	0.25 L Amber Jar	<4°C, freeze on lab arrival	4 d
Sediment	Munitions Constituents[2]	Modified EPA 8330 GC/MS[3]	0.25 L Amber Jar	<4°C, freeze on lab arrival	14 d
	TOC	Loss on Ignition	0.25 L glass jar	<4°C	14 d
	Grain size	ASTM Method D422	1 gallon Ziploc® bag	<4°C	14 d

[1]Preservatives are not required for these samples; however, all samples were stored and shipped at <4°C.

[2]TNT, TNB, DNB, 2-ADNT, 4-ADNT, DANT, 2,4-DNT, 2,6-DNT, RDX, 3,5-DNANIL, picric acid

[3]GC/MS is based on EPA 8095 modified to use mass spectrometry with negative chemical ionization.

[4]Grab and porewater samples collected from Vieques were extracted within 24 h of collection.

Analytical methods including instrumentation, quality assurance samples, decontamination procedures, sample documentation, and analytical data management and analysis are provided here. Similar details are elaborated upon or referenced in previous sections and in Appendix E.

- **Instrumentation:** Precision and accuracy of all laboratory analytical data were monitored throughout the analytical process. Instrument precision and accuracy of the GC/MS was assured by conducting initial calibration curves ($r^2 > 0.98$), and continuing calibration verification at a frequency of 10%. Calibration and maintenance of the MS was conducted prior to every analytical run including checking the accuracy of the tune and checking for leaks. Internal calibration was performed using stable isotope PAHs.

- **Quality Assurance Samples:** For each sampling trip, a blank passive sampler (field blank) was subjected to all phases of the field and transport experience. These samples were extracted and analyzed along with field samples in an effort to check for contamination. Extraction and procedural efficiency was measured using surrogates in each sample. Procedural blanks, spikes, and spike duplicates were conducted at a frequency of 5% of samples extracted.

- **Decontamination:** POCIS samplers are discrete units and typical sampling gear is not necessary to avoid cross contamination. On recovery each sampler was placed into Ziploc® bags and put on ice. At Camp Garcia, each canister was processed by removing each of the three samplers and individually wrapping in its own small Ziploc® bag, wrapped in bubble wrap, and then the three

replicates sealed in a second large Ziploc®, to minimize any chance of cross contamination among samplers. In the laboratory, samplers were dismantled on new, solvent washed foil and extracted in triple-rinsed and solvent washed extraction tubes.

- **Sample Documentation:** Chain of custody forms were originated upon collection of samples and followed the samples through processing at OSU and ERDC. Samples were labeled using water-proof labels and markers. Labels included date, field ID of sample, type of sample, and collecting scientist. Data from all field efforts were recorded in logbooks along with any notes and ancillary data. In both the field and the laboratory, extraction and analysis were recorded in laboratory notebooks and bound datasheets. Data were then transferred to spreadsheets that are backed up to secure servers.

- **Data Management and Analysis:** All laboratory data were stored in electronic form in more than one location. Analytical data from the laboratory were reported using spreadsheets. Data were not reported to other investigators or used for further calculations. Any data failing to pass criteria (associated blanks have positive hits, spikes are outside of range) resulted in the data being clearly noted with the data when reported.

Additional details describing the handling and QA/QC of samples are provided in Appendix E.

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 Eqn. 1 from the best available sampling rates (summarized in the accompanying ESTCP Guidance Document), the time (t) of deployment (days), and the mass of analyte accumulated by the sampler, (N):

$$C_w = \frac{N}{R_s t} \qquad \text{Eqn. 1}$$

Additional information on QA/QC is provided in Appendix E.

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, National Marine Fisheries Service (NMFS), the Puerto Rico Environmental Quality Board (PREQB), the Puerto Rico Department of Natural and environmental Resources (PRDNER), the USACE, USEPA Region 2, and United States Fish and Wildlife Service (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. That letter is in Appendix F. 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. Further, because no biota were sampled, previous discussions regarding collection permits for biota were not required. Vessel strike avoidance measures (NMFS, 2008; Appendix F) were followed to reduce the risk associated with disturbance of protected species including marine mammals, including manatees, and sea turtles. Diane Wehner (NOAA OR&R) was also on-site during sampler deployment to oversee any potential issues associated with endangered or threatened coral or other invertebrate species.

Experimental and dive plans for this work were vetted by NOSSA and internal Navy offices to ensure explosive safety considerations were adhered to (select documentation provided in Appendix F). Sampling only occurred at locations that MR divers had cleared for safety purposes, and scientific divers had assessed for environmental concerns.

5.7 SAMPLING RESULTS

The positive control field study at Santa Rosa Sound, FL and the technology optimization flume studies are summarized briefly in Section 2.2, and are provided in detail in Appendices B, C, and D. An overview of those studies is also included in Rosen et al. (2016). 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. The assembly at Station T4 had moved towards the munition (butted up against it), while the assembly at Station T7 had been dragged, apparently by surge at that station, about 18" beyond the placement location. All 90 samplers (3 per canister) were intact and had relatively little fouling. Examples of deployment and recovery conditions are shown in Figure 5-13, and are provided for all items in Appendix G. Representative condition of the membranes are shown in Figure 5-14. A few of the samplers showed evidence of ring-fastener associated corrosion along the perimeter of the membrane.

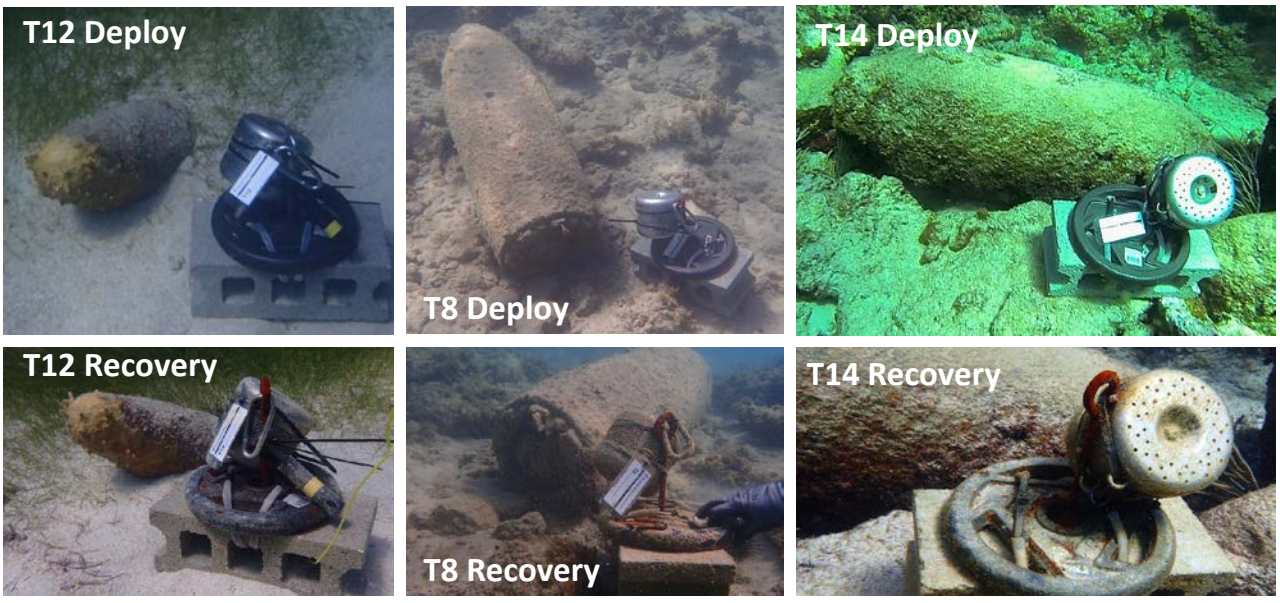

Figure 5-13. Representative target items and POCIS on deployment (top) and on recovery (below) after approximately 3 weeks. All stations are shown in Appendix G.

Figure 5-14. Representative appearance of sampler membranes after 19–23 days of deployment.

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. POCIS-derived water concentrations are provided in Table 5-8 (Target) and Table 5-9 (Grid). Grab samples, collected only at the 15 Target stations are shown in Table 5-10 (Initial) and Table 5-11 (Final). For POCIS, TNT, 2,4-DNT, DNB, RDX, 4-ADNT, 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 TNB were detected at one or more stations.

Picric acid, primarily used during the World War I era as a high explosive (a component of Explosive D, or ammonium picrate), and later favored for TNT, was analyzed for Initial Target grab samples only (N = 15) in response to site-specific interests. Sorbents other than HLB might be useful for quantifying picric acid using POCIS, but this was not the objective of this work, and would require further study. For picric acid, a second amber sampling bottle (volume 500 mL) was collected concurrently with the 1-L bottle for the primary MC list. Picric acid was analyzed by EPA 8330 as modified by Thorne and Jenkins (1995) (see Appendix E).

Table 5-8. POCIS-derived estimated water concentrations from 15 Target stations deployed at Bahia Salina del Sur in January 2016. Dark shaded values are above the QL, light shaded are above the MDL. Values in italics are number days samplers exposed at site.

	POCIS-derived Time-averaged concentration (ng/L)															
			Station ID													
	MDL	QL	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15
Analyte			*20*	*20*	*20*	*20*	*20*	*20*	*20*	*20*	*20*	*21*	*21*	*20*	*19*	*19*	*19*
TNB	1.9	5.7	0	0	0	0	Sample lost during lab prep	0	0	0	0	0	0	0	0	0	0
TNT	3.7	11.1	0	0	0	0		0	0	0	0	0	0	0	0	5304	0
2,6-DNT	1.4	4.3	0	0	0	0		0	0	0	0	0	0	0	0	0	0
2,4-DNT	6.6	19.9	0	0	0	0		0	0	0	0	0	0	0	0	46	0
DNB	6.0	17.9	0	0	0	0		0	0	0	0	0	0	0	0	0.0	0
RDX	2.9	8.8	8.4	5.1	5.0	7.6		6.6	7.1	12.6	11.1	11.6	6.6	7.9	0	0	0
4-ADNT	4.2	12.7	0	0	0	0		0	0	0	0	0	0	0	0	103	0
2-ADNT	2.6	7.7	0	0	0	0		0	0	0	0	0	0	5.2	0	54	0
3,5-DNANIL	1.7	5.0	0	0	0	0		0	0	0	0	0	0	0	0	6.3	0

For T14/15, MDL=1.5, 2.1, 0.7, 2.4, 1.0, 2.2, 1.2, 0.6, 0.6 ng/L for TNB, TNT, 2,6DNT, 2,4DNT, DNB, RDX, 4ADNT, 2ADNT, 3,5DNANL, respectively.
For T14/T15, QL= 4.4, 6.3, 2.0, 7.1, 2.9, 6.6, 3.6, 1.7, 1.7 ng/L for TNB, TNT, 2,6DNT, 2,4DNT, DNB, RDX, 4ADNT, 2ADNT, 3,5DNANL, respectively.

Table 5-9. POCIS-derived water concentrations from 15 Grid stations deployed at Bahia Salina del Sur in January 2016. Dark shaded values are above the QL, light shaded are above the MDL. Values in italics are number of days samplers exposed at site.

	POCIS-derived Time-averaged concentration (ng/L)																
	MDL	QL	A1	A2	A3	A4	B1	B2	B3	B4	C2	C3	C4	C5	D3	D4	D5
Analyte			*20*	*19*	*23*	*23*	*23*	*23*	*23*	*23*	*20*	*20*	*20*	*21*	*19*	*19*	*19*
TNB	1.9	5.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TNT	3.7	11.1	0	0	0	0	0	0	0	0	0	0	0	0	9.6	0	0
2,6-DNT	1.4	4.3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2,4-DNT	6.6	19.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DNB	6.0	17.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RDX	2.9	8.8	12.2	4.0	0	6.8	6.4	0	0	6.7	0	0	0	6.8	0	0	0
4-ADNT	4.2	12.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2-ADNT	2.6	7.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3,5-DNANIL	1.7	5.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 5-10. Grab water concentrations from 15 Target stations adjacent to POCIS on sampler Deployment (Initial). Dark shaded values are above the QL, light shaded are above the MDL.

	Grab water - Initial (ng/L)																
Analyte	MDL	QL	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15
TNB	3	9	0	0	0	0	0	0	0	0	0	0	0	0	0	22	0
TNT	8	25	0	0	0	0	0	0	0	0	0	0	0	0	0	4470	0
2,6-DNT	3	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2,4-DNT	9	28	0	0	0	0	0	0	0	0	0	0	0	0	0	13	0
DNB	6	17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RDX	18	54	0	0	0	0	51	0	0	0	0	26	24	0	0	0	0
4-ADNT	8	25	0	0	0	0	0	0	0	0	0	0	0	0	0	19	0
2-ADNT	6	17	0	0	0	0	0	0	0	0	0	0	0	0	0	31	0
3,5-DNANIL	12	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Picric Acid	166	500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

*Picric acid was not reported below QL based on analysical method

Table 5-11. Grab water concentrations from 15 Target stations adjacent to POCIS on sampler Recovery (Final). Dark shaded values are above the QL, light shaded are above the MDL.

	Grab water - Final (ng/L)																
Analyte	MDL	QL	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15
TNB	3	9	0	0	0	0	0	0	0	0	0	0	0	0	0	35	0
TNT	8	25	0	0	0	0	0	0	0	0	0	0	0	0	0	7497	0
2,6-DNT	3	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2,4-DNT	9	28	0	0	0	0	0	0	0	0	0	0	0	0	0	17	0
DNB	6	17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RDX	18	54	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4-ADNT	8	25	0	0	0	0	0	0	0	0	0	0	0	0	0	73	0
2-ADNT	6	17	0	0	0	0	0	0	0	0	0	0	0	0	0	89	0
3,5-DNANIL	12	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

5.7.3 Detection Frequency and Magnitude at Target Stations

5.7.3.1 TNT and other nitroaromatic compounds

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 5-12 at Target stations, Station T14 represented the highest concentration for all MC in the study for both POCIS and grab samples. Station T14 was the only Target station where TNT and other nitroaromatics, including TNT degradation products, were detected.

Table 5-12. Detection frequencies for POCIS and the two Grab time points for TNT and RDX at Target stations.

Sample Type	Constiuent	# Samples	# Defects	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” 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. Figure 5-15 and Table 5-11 show the POCIS and grab water TNT concentrations observed for water sampled at T14. 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 3-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. The closest sampling location to station T14 was station T15, where an apparently intact 1,000-lb GP bomb was present. This station, approximately 50 m away from T14, was below detection limits for all MC quantified.

Although T14 presented the highest water concentrations in the study for nitroaromatics, RDX was not detected by either POCIS or grab samples at that station (Table 5-9, Table 5-10, and Table 5-11) It is interesting to note that although RDX was not detected at 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.

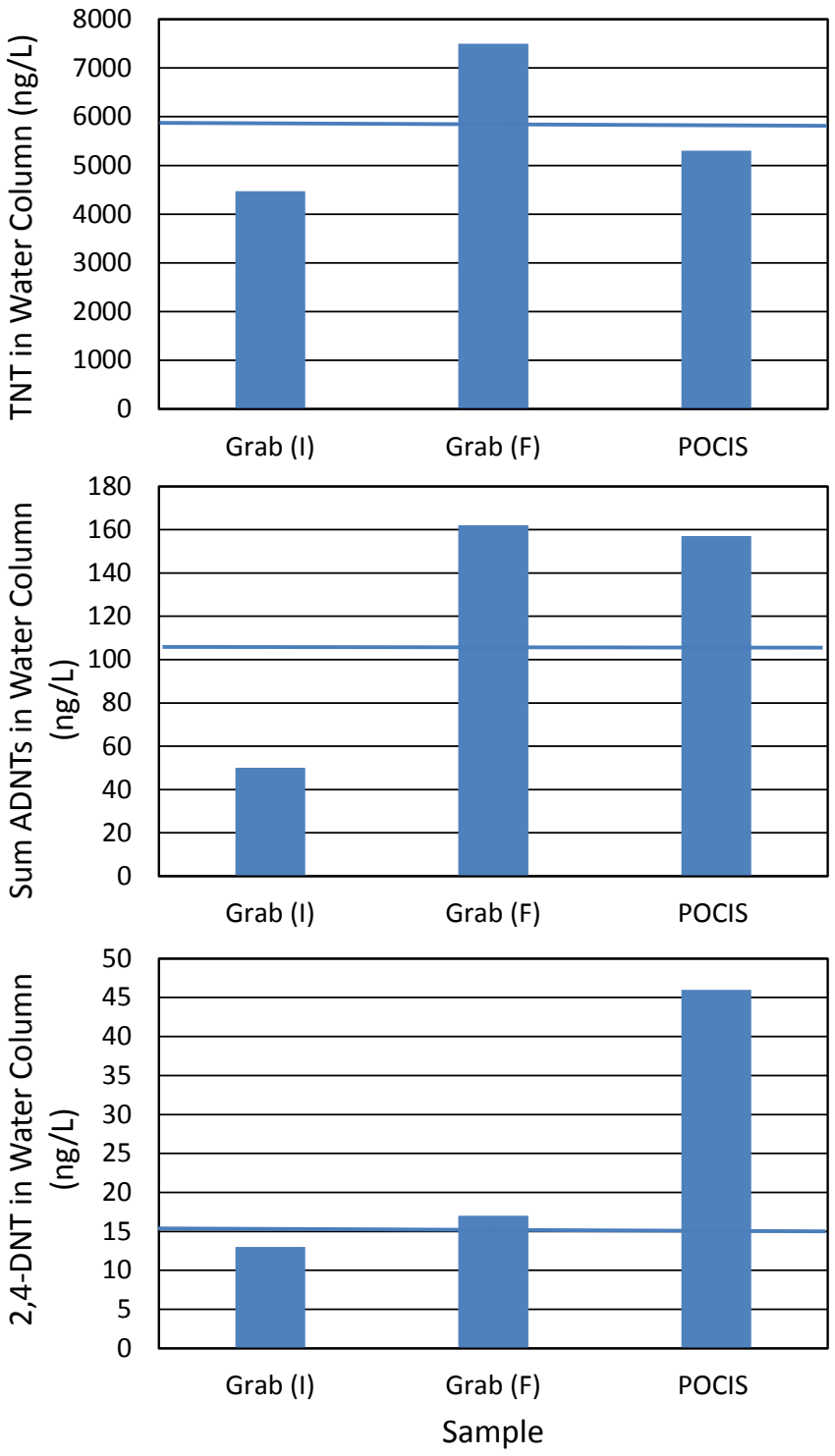

Figure 5-15. TNT (top), sum ADNTs (middle), and 2,4-DNT (bottom) water concentration at station T14 from initial grab (I), final grab (F), and POCIS. The blue line represents the average of the initial and final grab sample concentrations.

5.7.3.2 RDX

RDX concentrations at BSS ranged from 5–13 ng/L (when detected by POCIS; Table 5-8, and Table 5-9) and 24–51 ng/L (when detected in grabs collected during the deployment; Table 5-10. During the recovery process, all RDX grab water samples were non-detect (Table 5-11).

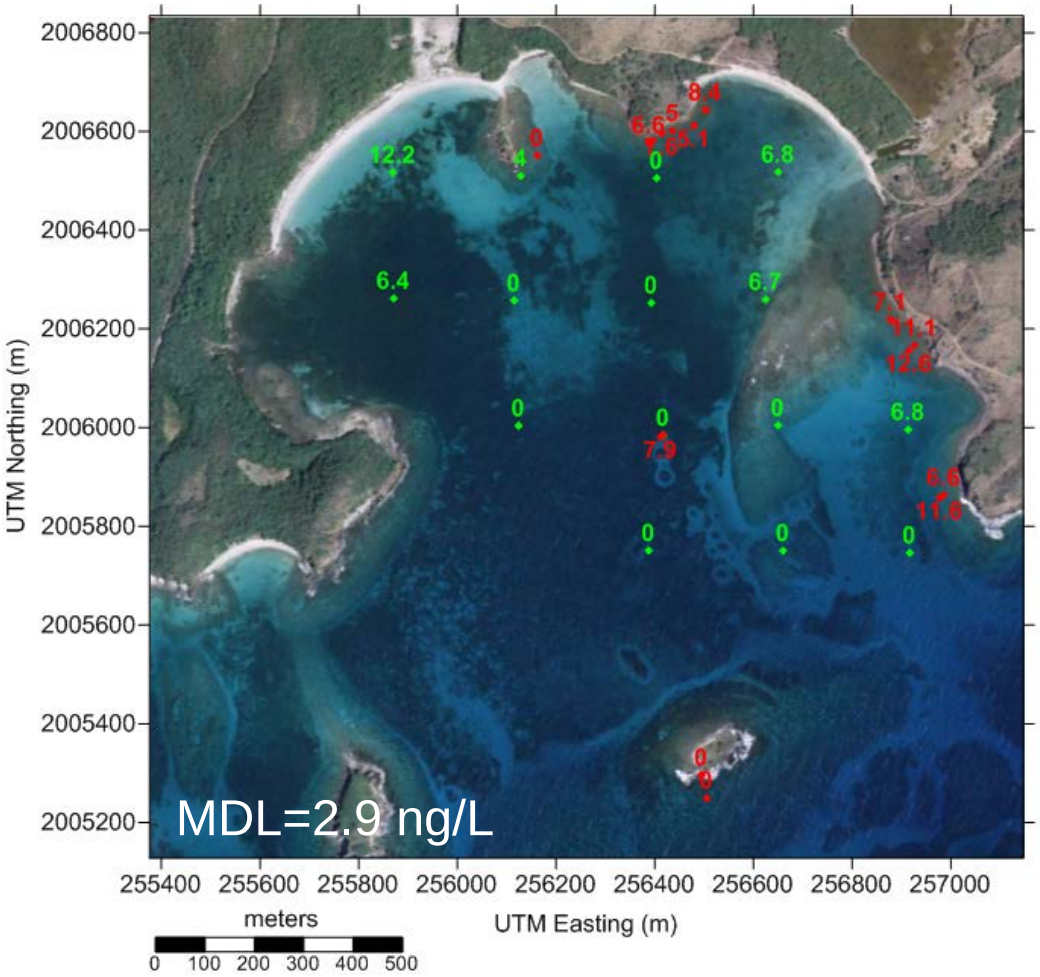

Figure 5-16. POCIS-derived TWA concentrations derived for RDX at 30 stations evaluated at Bahia Salina del Sur, based on method detection limits (MDL).

5.7.4 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 5-13.

Table 5-13. Detection frequencies of TNT and RDX for POCIS at Target and Grid Stations.

Sample Type	Constiuent	# Samples	# Defects	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

5.7.4.1 TNT

Only one TNT detect was observed for each 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 U.S. Navy target ship; Deslarzes, Nawojchik, and Evans, 2002).

5.7.4.2 RDX

Detection frequency was nearly twice as high for Target stations in comparison to Grid stations (79 and 40%, respectively). The concentration ranges were very similar, ranging from 5.0–12.6 (mean = 8.1) and 4.0–12.2 (mean = 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.

5.7.5 Site-Specific Current Velocities and POCIS Sampling Rates

The Nortek™ current profiler (see Section 5.5.4) results from opportunistic sampling during POCIS deployment and recovery efforts are provided in Table 5-14.

The overall mean (s.d.) from Stations inside the Bay were 5.10 (1.71) cm/s. Due to some uncertainty associated with not being able to continuously monitor current velocity at all stations for the duration of the exposure period, this average value for inside the Bay was used to represent the prevailing condition inside the Bay. The two stations south of Roca Alcatraz (Figure 5-16) provided outlying current data averaging 13.3 cm/s, therefore, sampling rates (Rs) were calculated based on current velocity curves fitted from the flume studies for inside the bay and outside the bay, which are reflected in Table 5-15.

Table 5-14. Current velocity (mean and standard deviations) from deployments of a Nortek® current profiler at representative stations during deployment and recovery.

	Date	Station ID	N	Mean	s.d.
Deployment	1/11/2016	A3	84	5.29	2.78
	1/11/2016	A4	144	5.59	2.53
	1/11/2016	B2	108	5.88	3.64
	1/11/2016	B3	108	5.65	2.81
	1/11/2016	B4	153	6.67	3.49
	1/12/2016	A1/A2/B1	3756	7.91	4.89
	1/13/2016	C5	1140	4.35	2.86
	1/13/2016	T12/C3	2196	6.54	4.00
	1/14/2016	D3	1200	4.80	2.53
Recovery	2/1/2016	A1/A2/B1	1104	4.63	3.43
	2/1/2016	A3	1678	2.18	1.09
	2/2/2016	T12	11700	6.65	3.77
	2/2/2016	T14/T15	3180	13.13	6.80
	2/3/2016	C5	1296	2.86	1.57
	2/3/2016	C3	204	2.38	1.25

Current velocity (cm/s)

Table 5-15. Sampling rates (L/d) used for calculation the TWA MC concentration at Vieques, derived using site-specific current velocities as derived in the ER-201433 Technology User's Guide (Appendix H).

	POCIS Sampling Rates (L/d)	
	Station Location	
Analyte	**T14&T15**	**All others**
TNB	0.329	0.077
TNT	0.185	0.105
2,6-DNT	0.133	0.085
2,4-DNT	0.133	0.066
DNB	0.274	0.045
RDX	0.377	0.284
4-ADNT	0.324	0.093
2-ADNT	0.474	0.104
3,5-DNANIL	0.339	0.05

5.7.6 Water Quality Characteristics from Bahia Salina del Sur

Table 5-16 and Table 5-17 summarize basic water quality characteristics measured during the POCIS validation study. The Troll® 9500 data (temperature, pH, dissolved oxygen, salinity) were generally collected concurrently and at the same locations as current velocity data. The total suspended solids (TSS) and dissolved organic carbon (DOC) analyses were performed on discrete water samples collected concurrently with grab samples collected for MC analysis during the Recovery (February 2016) event. These data were reported for documentation purposes only.

Table 5-16. Summary of water quality parameters collected 1 foot above the sea floor at select stations using a Troll® 9500 logging device.

			Sampling Duration	Temp (°C)		pH		D.O. (mg/L)		Salinity (psu)	
	Date	Station ID	(min)	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Deployment	11-Jan-16	A3	34	27.9	0.01	8.23	0.00	7.0	0.13	33.0	0.12
	11-Jan-16	A4	34	28.0	0.01	8.20	0.01	6.5	0.07	33.2	0.01
	11-Jan-16	B2	34	27.6	0.01	7.89	0.41	6.1	0.03	33.3	0.18
	11-Jan-16	B3	32	27.7	0.02	8.19	0.03	6.6	0.12	33.5	0.05
	11-Jan-16	B4	36	28.2	0.11	8.29	0.02	8.2	0.16	33.4	0.03
	12-Jan-16	A1/A2/B1	336	27.5	0.14	8.24	0.03	6.4	0.74	33.2	0.08
	13-Jan-16	C5	120	26.8	0.07	8.19	0.03	5.5	0.19	33.1	0.18
	13-Jan-16	T12/C3	208	27.4	0.07	8.24	0.00	6.6	0.12	32.9	0.04
	14-Jan-16	D3	122	27.1	0.06	8.24	0.02	6.3	0.10	32.8	0.02
Recovery	1-Feb-16	A1/A2/B1	114	27.1	0.03	8.22	0.00	6.3	0.05	34.2	0.01
	1-Feb-16	A3	162	26.6	0.10	8.19	0.10	6.3	0.28	34.0	0.20
	2-Feb-16	T12	215	26.9	0.09	8.25	0.01	6.8	0.22	34.1	0.03
	2-Feb-16	T14/T15	73	26.9	0.02	8.22	0.02	5.9	0.03	34.2	0.06
	3-Feb-16	C5	131	26.8	0.05	8.22	0.01	6.1	0.18	34.0	0.05
	3-Feb-16	D3	41	26.9	0.02	8.25	0.01	6.7	0.19	33.9	0.03

Table 5-17. TSS and DOC concentrations from the POCIS Recovery phase at BSS.

	mg/L	
Station ID	DOC	TSS
T8	0.8	11.0
T11	1.0	12.5
T12	0.8	8.5
T13	1.0	14.7
T15	1.0	8.1

Pore Water and Sediment Sampling Results

All porewater and sediment samples were below method detection limits, which are provided in Table 5-18. Sample IDs correspond with the four POCIS sampling locations selected for further evaluation (A1, T10, T11, T12), and whether or not the location was at inside (~ 0.5 m) or outer (~ 1.5 to 2 m) collection locations (e.g., A1–IC corresponds with Station A1, Inner Composite) around the munition or center point of the grid station. The sampling design for porewater and surface sediment are provided in Section 5.5.6. 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. The sediment organic carbon and grain size distributions for the focused sediment and porewater sampling study are provided in Table 5-22.

Table 5-18. Porewater MC concentrations collected from BSS.

	Pore water (ng/L)									
Analyte	**MDL**	**QL**	**A1-IC**	**T10-IC**	**T11-IC**	**T12-IC**	**A1-OC**	**T10-OC**	**T11-OC**	**T12-OC**
TNB	3	9	0	0	0	0	0	0	0	0
TNT	8	25	0	0	0	0	0	0	0	0
2,6-DNT	3	8	0	0	0	0	0	0	0	0
2,4-DNT	9	28	0	0	0	0	0	0	0	0
DNB	6	17	0	0	0	0	0	0	0	0
RDX	18	54	0	0	0	0	0	0	0	0
4-ADNT	8	25	0	0	0	0	0	0	0	0
2-ADNT	6	17	0	0	0	0	0	0	0	0
3,5-DNANIL	12	36	0	0	0	0	0	0	0	0

Table 5-19. Surface sediment MC concentrations collected from BSS.

	Sediment Concentration (µg/kg), Dry weight									
Analyte	**MDL**	**QL**	**A1-IC**	**T10-IC**	**T11-IC**	**T12-IC**	**A1-OC**	**T10-OC**	**T11-OC**	**T12-OC**
TNB	0.6	1.8	0	0	0	0	0	0	0	0
TNT	1.6	4.8	0	0	0	0	0	0	0	0
2,6-DNT	0.5	1.5	0	0	0	0	0	0	0	0
2,4-DNT	1.8	5.4	0	0	0	0	0	0	0	0
DNB	1.1	3.3	0	0	0	0	0	0	0	0
RDX	3.4	10.2	0	0	0	0	0	0	0	0
4-ADNT	1.6	4.8	0	0	0	0	0	0	0	0
2-ADNT	1.1	3.3	0	0	0	0	0	0	0	0
3,5-DNANIL	2.3	6.9	0	0	0	0	0	0	0	0

Table 5-20. Total organic carbon (TOC) and grain size distribution from stations A1, T10, T11, and T12 at BSS.

	Grain size (%)			TOC
Sample ID	Gravel	Sand	Fines	(mg/L)
A1 Inner	0.0	90.0	10.0	0.62
A1 Outer	0.0	92.2	7.8	0.49
T10 Inner	7.6	87.4	5.0	1.26
T10 Outer	29.1	68.7	2.2	1.04
T11 Inner	6.5	91.2	2.3	0.65
T11 Outer	11.5	86.4	2.1	0.90
T12 Inner	1.6	96.1	2.3	1.04
T12 Outer	0.9	96.0	3.0	0.87

5.7.7 Quality Assurance and Quality Control (QA/QC)

All blanks, including grab water (n = 6, Table 5-21), porewater (n = 3), POCIS (n=3), and sediment (n = 3, Table 5-22) were below quantitation limits. Extraction recoveries for laboratory and matrix spikes were acceptable for all matrices as well. Efficiencies for grab water and sediment samples are provided in Tables 5-23 and 5-24, respectively. Extraction efficiencies from POCIS (spiked HLB adsorbant) ranged from 95–120% and RSDs were less than 10% for each analyte. Mean extraction efficiency from pore-water ranged from 76–105 and RPD values were less than 20% (n = 2 for each matrix). All sampling holding and instruments quality control criteria was met. Water samples were extracted in the field to obtain less than a 48 hour holding time.

Table 5-21. QA/QC samples showing laboratory blank, field laboratory blanks (n = 3), field blank, and open water blanks.

	Grab Water (ng/L)						
Analyte	**QL**	**LB 1**	**FLB 1**	**FLB 2**	**FLB 3**	**FB**	**OWB**
TNB	9	0	0	0	0	0	0
TNT	25	0	0	0	0	0	0
2,6-DNT	8	0	0	0	0	0	0
2,4-DNT	28	0	0	0	0	0	0
DNB	17	0	0	0	0	0	0
RDX	54	0	0	0	0	0	0
4-ADNT	25	0	0	0	0	0	0
2-ADNT	17	0	0	0	0	0	0
3,5-DNANIL	36	0	0	0	0	0	0

LB = Analytical laboratory blank; FLB = Field laboratory blank (replicate);

Field Blank= clean water transported in field; OWB= Open Water Blank (collected from outer bay in field)

Table 5-22. QA/QC samples showing laboratory blanks for sediment (n = 3).

	Sediment- Final (ug/kg)				
Analyte	**MDL**	**QL**	**LB A**	**LB B**	**LB C**
TNB	0.6	1.8	0	0	0
TNT	1.6	4.8	0	0	0
2,6-DNT	0.5	1.5	0	0	0
2,4-DNT	1.8	5.4	0	0	0
DNB	1.1	3.3	0	0	0
RDX	3.4	10.2	0	0	0
4-ADNT	1.6	4.8	0	0	0
2-ADNT	1.1	3.3	0	0	0
3,5-DNANIL	2.3	6.9	0	0	0

LB = Analytical laboratory blank;

Table 5-23. QA/QC samples showing recoveries for laboratory spiked reagent water and recoveries and relative percent differences from field spiked water collected outside Bahia Salina del Sur.

Analyte	Laboratory Spiked Reagent Water#		Field Spiked Open Water*	
	Mean, % Recovery	SD	Mean, % Recovery	RPD
TNB	93	1	88	15
TNT	107	7	94	11
2,6-DNT	105	4	87	18
2,4-DNT	102	4	94	15
DNB	101	6	84	13
RDX	93	2	95	0
4-ADNT	81	2	89	5
2-ADNT	88	4	89	0
3,5-DNANIL	76	6	86	1

n=4

* n=2, RPD - Relative Percent Difference

Table 5-24. QA/QC samples showing laboratory blanks for laboratory sediments (sand; n = 3).

Analyte	Laboratory Spiked Sediment (Sand)*	
	Mean, % Recovery	SD
TNB	73	3
TNT	82	4
2,6DNT	78	3
2, 4DNT	78	3
DNB	78	3
RDX	101	3
4ADNT	82	4
2ADNT	79	2
3,5DNANIL	87	4

*n = 4

5.7.8 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. In Table 5-25, Figure 5-17, Figure 5-18, concentrations for MC relative to the HC5 are provided. MC concentrations at BSS were generally 4 to 6 orders of magnitude (10,000 to 1,000,000 times) lower than the HC5. The single TNT value over the quantitation limit 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 (Section 2-2.2; Appendix B) were 4 and 6 orders of magnitude lower than effects based HC5 values, similar to those observed at BSS.

Table 5-25. 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

HC5: Hazardous concentration for 5% of species (from Lotufo et al., 2017)

NA: Fewer than six species. No calculation available.

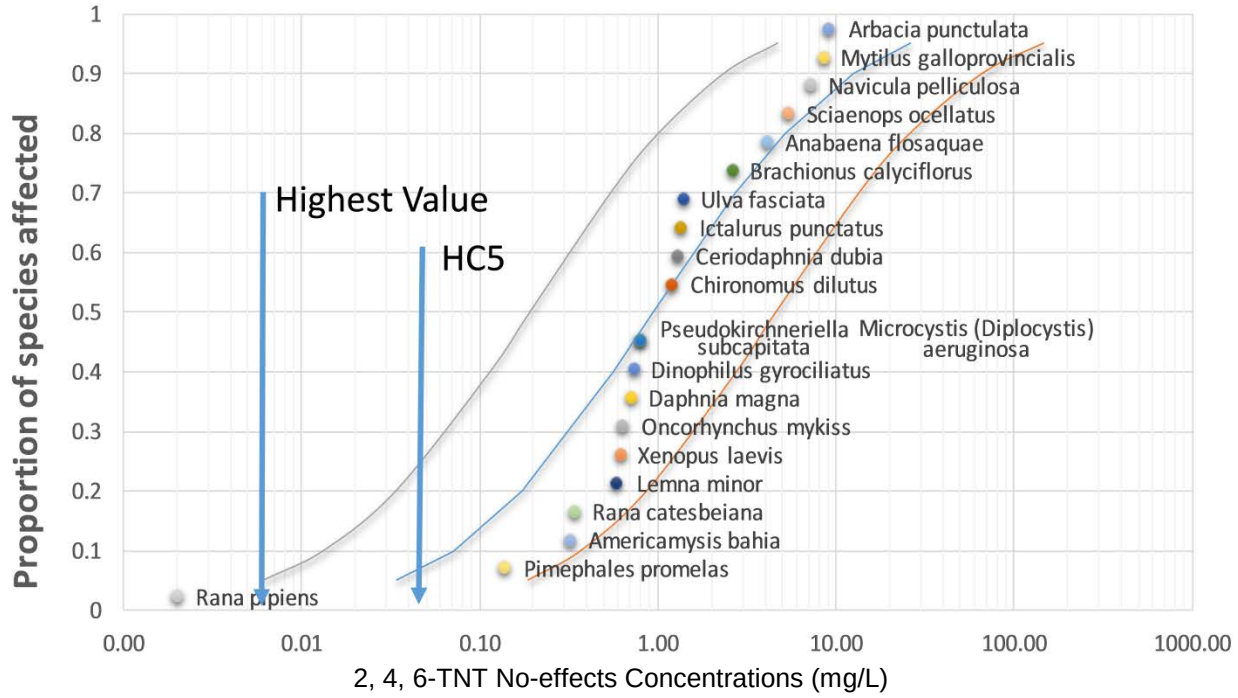

Figure 5-17. Comparison of TNT no effects-based HC5 and concentrations measured at Bahia Salina del Sur. Note that concentrations are on a log-scale.

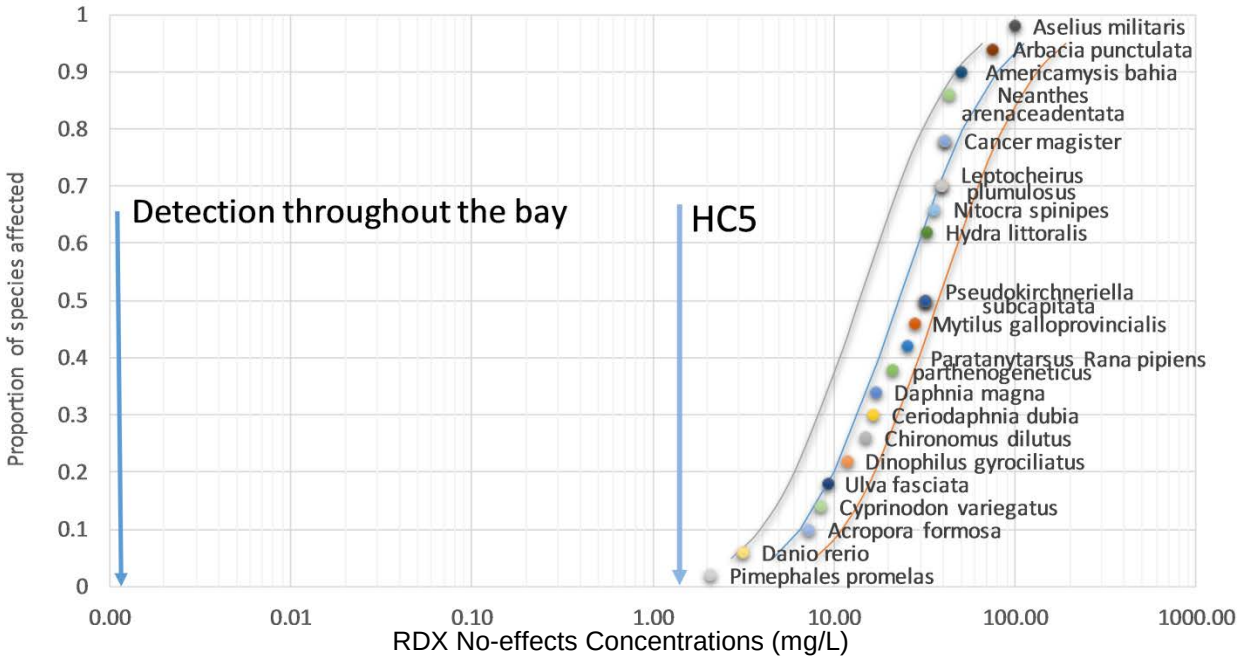

Figure 5-18. Comparison of RDX no effects-based HC5 and concentrations measured at Bahia Salina del Sur. Note that concentrations are on a log-scale.

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 munitions constituents (MC) in a positive control field study at a clean site. Following permit approvals, 15 grams of Composition 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 Time-Weighted Average 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 Composition B flume study, the positive control field study, and the Vieques field validation study. Composition B flume-deployed POCIS estimated TWA water concentrations for TNT and RDX that were similar to averaged concentrations generated using multiple grab TWA concentrations. The highest ratio of the POCIS-derived and the grab-sample-derived averages was only 1.44. In the positive control field study, MC concentration successfully determined using POCIS (TWA water concentrations 0.3–2.0 m from source, 9–103 ng/L for TNT, and 9– 97 ng/L, for RDX) could not be compared to discrete-sampling-derived concentrations as grab water samples resulted only in non-detects. When considering the QL for grab samples (50 and 120 ng/L for TNT and RDX, respectively), grab sample data provide some level of validation of the POCIS-derived data. In the Vieques field validation study, one 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 (5,984 ng/L) at the station was only 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. POCIS-derived average RDX concentrations ranged narrowly from 5–13 ng/L (average = 8 ng/L) for 11 stations with detectable concentrations. Only three stations had detectable concentration from grab samples during the initial period, and all stations had concentrations reported as non-detects for the final period. The three reported concentrations for the initial period were 24, 26, and 51 ng/L. When considered along with the non-detects reported for the final period, average concentrations estimated using POCIS and two grab samples were similar. 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 sampler would detect MC at levels substantially lower than achievable using typical grab sampling methods. 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. Detection limits for POCIS-derived TWA concentrations and grab water samples are generally comparable when the volume of water volume of water cleared of MC for both methods is comparable (e.g., 3-week POCIS deployment and 10 L of grab water sample). For the Comp. B positive control study, the concentrations of TNT and RDX in grab samples taken at three different time points adjacent to the source were reported as non-detects; contrastingly, POCIS-derived TWA concentrations were reported for 12 out of 20 stations, including those more distant from the source than the point of grab water sampling. 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. For the Vieques field validation study, the concentrations of RDX in the initial grab samples were reported as non-detects for 3 out of 15 stations (detection frequency = 20%), while for final grab samples RDX was reported as non-detects for all stations (detection frequency = 0). Contrastingly, POCIS-derived TWA concentrations were reported for 11 out of 14 stations (detection frequency = 79%).

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. A total of 20, 51, and 30 POCIS canisters (each containing three 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 method detection limits, 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 (Section 2.2; Appendix D) 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: Quality Control and Quality Assurance

Performance objective #6 was the demonstration that all field and laboratory efforts followed experiment-specific quality assurance objectives and that quality control criteria were met. All criteria were met for this part of the project. Blanks, including field and laboratory, did not have MCs

above the quantitation limits. All spike tests had accuracy and relative precision within 25% of expected. In addition, all other sampling handling and instrument criteria were also met.

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 to 1,000,000 times lower than hazardous concentrations to 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, 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.

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 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 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 don't degrade (e.g., freeze or extract samples daily). Laboratory feedback indicated that processing of POCIS in comparison with standard solid-phase extraction (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. 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 (Section 7), 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 of 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 POCIS would help with the criticisms of sampling at the wrong time, at the wrong place, was seen as a primary advantage for the Gulf Breeze study. Site managers on Vieqees 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), 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 on study objectives. Cost scenarios to develop integrative samples with POCIS in comparison to other means are described in Section 7.

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 throughout BSS for a period of 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 and costs associated with accessing the site with munitions response and scientific divers. Note that costs associated with other tasks from this project, including the positive control field validation, are not included here. The costs associated with POCIS and grab sampling of water for MC analysis includes placement and monitoring costs for the demonstration project (Table 7-1). Field work costs below do not include management, oversight, and coordination. Uncertainties in applying this cost estimate for POCIS application depend on safety requirements on a site-specific basis.

Table 7-1. Cost model for demonstration of POCIS at Bahia Salina del Sur.

Cost Element	Placement and Modeling Services	Costs ($)
Site Visit	NAVFAC managerial and technical support	5,625
	ESTCP technical personnel	4,500
	Total	10,125
Sampling Plan	Sampling design, QA/QC, permits	30,000
	Total	30,000
Reconnaissance Survey	Dive Support (3 munitions response + 2 scientific divers)	15,000
	Boat rental (Qty 2)	5,200
	NAVFAC technical support	9,375
	Review with ESTCP technical team	5,000
	Total	34,575
Anchoring Study	Dive Support (3 munitions response + 2 scientific divers)	11,250
	Boat rental (Qty 2)	2,600
	NAVFAC technical support	6,750
	Data Review with ESTCP technical team	5,000
	Equipment and consumables	2,000
	Total	27,600

Table 7-1. Cost model for demonstration of POCIS at Bahia Salina del Sur. (Continued)

Cost Element	Placement and Modeling Services	Costs ($)
Deployment	Dive Support (3 MR + 2 scientific divers)	22,500
	Boat rental (Qty 2)	7,800
	NAVFAC technical support	18,000
	Technical field team	22,500
	Current profiler/water quality logger rentals	1,500
	Equipment and consumables	22,650
	Shipping costs	2,500
	Total	97,450
Recovery	Dive support (3 MR + 2 scientific divers)	22,500
	Boat rental (Qty 2)	7,800
	NAVFAC technical support	12,000
	Technical field team	22,500
	Consumables	3,500
	Shipping costs	1,500
	Total	69,800
Sediment and Porewater Sampling	Dive Support (3 MR + 2 scientific divers)	7,500
	Boat rental (Qty 2)	2,600
	NAVFAC technical support	6,750
	Technical field team	12,000
	Consumables	2,000
	Shipping	500
	Total	31,350
Chemical Analysis	POCIS, grab water, sediment, porewater and ancillary measurements (TOC/DOC, TSS, grain size)	28,400
	Total	28,400
Reporting	Reports to NAVFAC and ESTCP	40,000
	Total	40,000
	Vieques Demonstration Total	369,300

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 to other projects with similar requirements (e.g., MR and scientific divers) is presented in Table 7-2.

Table 7-2. Cost model for implementation of POCIS at a UWMM site for 15 monitoring locations.

Cost Element	POC IS Implementation Support	Costs ($)
Site Visit	DoD Remedial Program Manager	5,625
	Technical personnel	4,500
	Total	10,125
Deployment	Dive support (3 MR + 2 scientific divers)	15,000
	Boat rental (Qty 2)	5,200
	Site support	6,000
	Technical field team	12,000
	Sampling plan/logistics/permits	20,000
	Current profiler/water quality logger rentals	1,500
	Equipment and consumables	13,515
	Shipping costs	1,500
	Total	74,715
Recovery	Dive Support (3 MR + 2 scientific divers)	15,000
	Boat rental (Qty 2)	5,200
	Site support	6,000
	Technical field team	12,000
	Consumables	1,500
	Shipping costs	1,500
	Total	41,200
Chemical Analysis	MC and ancillary (e.g., DOC, TSS)	9,500
	Total	9,500
Reporting	Report to DoD site manager	20,000
	Total	20,000
	Implementation Total	155,540

7.1.3 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 literally 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 we have 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 costs 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 munitions response (MR) divers and two scientific divers were required to execute the demonstration.

Comparative sampling: The integrative nature of POCIS, continuously sampling over 2 or 3 weeks, distinctly contrasts with grab sampling that captures one point in time. Therefore, grab sampling is not an equal comparison to passive samplers such as POCIS. Autosamplers, such as Teledyne ISCO samplers, commonly used to collect representative samples for stormwater monitoring and compliance, are a more logical technology for comparison with POCIS than status quo grab sampling. However, because nitroaromatics degrade rapidly and need to be frozen or extracted as soon as practical, autosampler bottles would have to be changed out daily to preserve the integrity of the samples, requiring many more visits to the site. Further ISCO samplers typically require regular maintenance while the POCIS is maintenance-free while deployed. Finally, costs can vary significantly based on the complexity of the site, including considerations for bathymetry, currents, infrastructure, and other considerations, as well, as site access and logistical considerations.

7.2 COST ANALYSIS

To evaluate and compare the costs of integrative water sampling with POCIS with alternative approaches (e.g., composite or grab sampling), three scenarios are 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 six 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.

7.2.1 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 or munitions debris, and items of relatively unknown condition are widely present throughout the bay. The approach involves an unbiased (aka Grid) design incorporating 15 stations approximately equidistant from one another for a 2-week exposure. The costs associated with Site 1 are already presented in Table 7-2, totaling $155,540. 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.

7.2.1.1 Grab Sampling

As discussed previously, grab sampling and integrative sampling with passive samplers are inherently different. For sites (e.g., Vieques) already undergoing the CERCLA process with single grab sampling requirements indicating no ecological risk, a comparison of POCIS with repeated grab sampling is not necessary. For sites where risk is less clear, we provide a comparison between POCIS and multiple grab sampling that would be required to provide an integrative sample. 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 composite sample somewhat representative of an “integrated” sample. However, this approach 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 explosive ordnance detection (EOD) technician would be required to be on site.

The sampling still require two boats, a sampling boat and a support boat, and would require 14 consecutive days of travel to and from the site for a smaller project team. The costs of this scenario equates to $239,740 (Table 7-3), a 54% increase over POCIS deployments with a full dive crew.

7.2.1.2 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.

Table 7-3. Site 1 cost comparison.

Cost Element	Description	POCIS ($)	Grab ($)
Site Visit	DoD site managers	5,625	5,625
	Technical Personnel	4,500	4,500
	Total	10,125	10,125
Deployment	MR diver or EOD support	15,000	24,000
	Boat rental	5,200	41,600
	Site support	6,000	48,000
	Technical field team	12,000	48,000
	Sampling plan/logistics/permits	20,000	20,000
	Current profiler/water quality logger rentals	1,500	1,500
	Equipment and consumables	13,515	13,515
	Shipping costs	1,500	3,500
	Total	74,715	200,115
Recovery	Dive support (3 MR + 2 scientific divers)	15,000	N/A
	Boat rental	5,200	
	Site support	6,000	
	Technical field team	12,000	
	Consumables	1,500	
	Shipping costs	1,500	
	Total	41,200	
Chemical Analysis	MC and ancillary (e.g., DOC, TSS)	9,500	9,500
	Total	9,500	9,500
Reporting	Report to DoD site manager	20,000	20,000
	Total	20,000	20,000
	Grand Total	155,540	239,740

7.2.2 Site 2

Site 2 represents a 20-acre lagoon, also impacted by a former training range with numerous munitions known to be present from historical surveys. The study design involves a 2-week POCIS deployment within approximately 50 feet of the shoreline around the lagoon perimeter at a total of six 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 only for each deployment and recovery phases. The costs for a POCIS program at this site are estimated at $111,125 (Table 7-4).

7.2.2.1 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 on-site at minimum 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 only one boat would be required for this sampling effort. However, to be comparable with an integrated sample generated by POCIS, multiple grabs 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 (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 six 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 on-site 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 (Table 7-4).

Table 7-4. Site 2 cost comparison.

Cost Element	Description	POCIS ($)	Grab ($)	Composite ($)
Site Visit	DoD remedial project manager	5,625	5,625	5,625
	Technical personnel	4,500	4,500	4,500
	Total	10,125	10,125	10,125
Autosampler Install	Installation (6 samplers)	-	-	15,000
Deployment and Maintenance	MR diver or EOD support	7,500	24,000	7,500
	Boat rental	2,600	20,800	2,600
	Site Support	4,500	48,000	11,250
	Technical field team	9,000	48,000	48,000
	Planning/logistics/permits	20,000	20,000	20,000
	ISCO autosampler rentals (Qty 6)	-	-	9,000
	ISCO autosampler maintenance	-	-	6,000
	Current profiler/WQ logger rentals	1,500	1,500	1,500
	Equipment and consumables	6,500	13,515	14,000
	Shipping costs	1,500	3,500	5,500
	Total	53,100	179,315	140,350
Recovery	Dive support (3 MR + 2 scientific divers)	7500	N/A	7,500
	Boat rental (Qty 2)	2,600		2,600
	Site support	4,500		N/A
	Technical field team	12,000		
	Consumables	1,500		
	Shipping costs	1,500		
	Total	29,600		10,100
Chemical Analysis	MC and ancillary (e.g., DOC, TSS)	3,300	3,300	3,300
	Total	3,300	3,300	3,300
Reporting	Report to DoD site manager	15,000	15,000	15,000
	Total	15,000	15,000	15,000
	Grand Total	111,125	207,740	178,875

*Anticipated that one boat would be sufficient for grab sampling from boat (no divers required).

7.2.3 Site 3

Site 3 is a bay where discarded military munitions (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) 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 to 5 feet above the sediment bed. A total of 10 POCIS canisters would be deployed at this site at 10 stations. The costs for a POCIS program at this site are estimated at $102,735.

7.2.3.1 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 grabs approximately 3 to 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 (Table 7-5), a 23% increase over POCIS deployments.

7.2.3.2 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 the majority of the field team will be on-site during the entire process, costs are primarily weighted towards the "Deployment and Maintenance" cost element. The cost of this scenario equates to $164,735 (Table 7-5), a 60% increase over POCIS deployments.

Table 7-5. Site 3 cost comparison.

Cost Element	Description	POCIS ($)	Grab ($)	Composite ($)
Site Visit	DoD remedial project manager	5,625	5,625	5,625
	Technical Personnel	4,500	4,500	4,500
	Total	10,125	10,125	10,125
Autosampler Install	Installation (10 samplers)	-	-	15,000
Deployment & Maintenance	Site support	6,000	6,000	6,000
	Technical field team	9,000	48,000	48,000
	Planning/logistics/permits	15,000	15,000	15,000
	ISCO autosampler rentals (Qty 10)	-	-	9,000
	ISCO autosampler maintenance	-	-	6,000
	Current Profiler/WQ logger rentals	1,500	1,500	1,500
	Equipment and consumables	11,110	13,515	14,000
	Shipping costs	1,500	3,500	5,500
	Total	44,110	83,110	121,110

Table 7-5. Site 3 cost comparison. (Continued)

Cost Element	Description	POCIS ($)	Grab ($)	Composite ($)
Recovery	Site support	6,000	6,000	6,000
	Technical field team	12,000	N/A	N/A
	Consumables	1,500		
	Shipping costs	1,500		
	Total	21,000	6,000	6,000
Chemical Analysis	MC and ancillary (e.g., DOC, TSS)	7,500	7,500	7,500
	Total	7,500	7,500	7,500
Reporting	Report to DoD site manager	20,000	20,000	20,000
	Total	20,000	20,000	20,000
Grand Total		102,735	126,735	164,735

8. IMPLEMENTATION ISSUES

The advantages of POCIS have been increasingly demonstrated over the past 10 to 15 years since early publications demonstrating their utility for monitoring polar and weakly hydrophobic organics (e.g., Alvarez, 2004; Harman, Allen, and Vermeirssen, 2012; Miege et al., 2012; Morin et al., 2012). 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, Debenest, and Delmas, 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 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 underwater military munitions (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 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 leave in place 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 sampling rate (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, Allen, and Vermeirssen, 2012). Efforts to improve the quantitative ability of POCIS are ongoing, including a recently completed SERDP SEED project (ER-2542) 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.

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APPENDIX A
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APPENDIX B
POSITIVE CONTROLLED FIELD STUDY RESULTS

FIELD VALIDATION OF AN INTEGRATIVE PASSIVE SAMPLER FOR USE AT UNDERWATER MUNITIONS SITES

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ABSTRACT

This study examined the viability of Polar Organic Chemical Integrative Samplers (POCIS) for detection and quantification of munitions constituents (MC), including trinitrotoluene (TNT), aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs), dinitrotoluene (DNT), and trinitrohexahydro-s-triazine (RDX) in a field setting. POCIS were deployed at varying distances from fragments (15 g total mass) of the explosive formulation Composition B (39.5% TNT, 59.5% RDX, and 1% wax binder) in an embayment of Santa Rosa Sound (Florida, USA). POCIS-derived time-weighted averaged (TWA) estimated water concentrations from a 13-day deployment ranged from 9-103 ng/L for TNT and RDX outside the source canister, with concentrations decreasing with increasing distance from the source to below quantitation limits (5.4-6.6 ng/L) 5 m away. Moderate fouling observed on POCIS membranes after 13-day led to a subsequent experiment to investigate the potential effects of biofouling on sampling rate for MC. Following conditioning periods of 0, 7, 14 or 28 day at the same field site, POCIS were transferred to aquaria spiked with MC for a 7-day exposure. No significant differences in sampling rate were observed among the different fouling time periods, although mass of fouling organisms on the membranes was statistically greater at 28 day field exposure compared to other time points. This study verifies the high sensitivity and integrative nature of POCIS for dominant conventional MC in estuarine environments, and suggests that application at military munitions sites will be useful for ecological risk assessment purposes.

Keywords: Munitions, POCIS, TNT, RDX, time-weighted average, passive sampling

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ETHICAL APPROVAL

All applicable national and institutional guidelines for the care and use of animals (i.e., oysters) were followed.

B1. INTRODUCTION

As a result of historic military activities, unexploded ordnance (UXO) and discarded military munitions (DMM) are present at underwater sites, and may still contain a variety of munitions constituents (MC) such as the high explosives, 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and their degradation products. Despite reports of underwater munitions and explosives of concern (MEC) corroding, breaching, and leaking MC into the water column (Darrach, Chutjian, and Plett, 1998; GMI, 2007; Lewis et al., 2009; Pascoe, Kroeger, Leisle, and Feldpausch, 2010; Porter, Barton, and Torres, 2011; Rosen et al., 2016), a number of challenges have prevented accurate assessment of environmental exposure using traditional water sampling and analysis techniques. These challenges include a high level of effort required to identify leaking underwater MEC, and to quantify MC at low concentrations (i.e., low ng/L) at meaningful locations from the source and/or over time (Darrach, Chutjian, and Plett, 1998; van Ham et al., 2002; Ochsenbein, Zeh, and Berset, 2008; National Defense Center 2010; Rosen et al., 2016).

Integrative passive sampling techniques, specifically Polar Organic Chemical Integrative Samplers (POCIS; Alvarez et al., 2004), have recently been demonstrated in laboratory-based experiments as a means of improving the environmental exposure assessment of MC (Belden et al., 2015). POCIS offer an advantageous alternative to traditional sampling methods (e.g., collection of discrete grab samples) at sites where fluctuation in concentrations or low-level concentrations are expected to occur, such as in the vicinity of underwater munitions. The continuous sampling approach of POCIS allows detection and identification of polar organics ($\log K_{ow} < 3$) in an integrative manner, providing time-weighted average (TWA) concentrations, and semi-quantitative estimates of waterborne chemicals at ultra-trace levels (Alvarez et al., 2004; Mazzella, Debenest, and Delmas, 2008).

Unlike samplers that rapidly achieve equilibrium using high surface area to sorbent volume, POCIS typically exhibit negligible loss rates and 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 the sample preparation by elimination of electrical or fuel powering requirements, significantly reducing the numbers of analyses required and providing protection of analytes against decomposition during transport and storage (Kot-Wasik et al., 2007). POCIS data can subsequently be used to assess MC exposure and associated potential for ecological risk based on propensity for uptake and toxicity to biota without having to make such measurements.

The purpose of this study was to validate the use of POCIS for low level MC detection and quantification in a marine/estuarine environment. The approach involved permitted placement of a known quantity of a common solid military formulation, Composition B (39.5% TNT, 59.5% RDX, and 1% wax binder), at a fixed location in Santa Rosa Sound, Florida. Target MC included parent compounds and the TNT degradation products aminodinitrotoluenes (ADNTs) and diaminonitrotoluenes (DANTs). To our knowledge, this study reports the first field application of POCIS for MC, and validates its applicability and advantage for inclusion in exposure assessments at underwater MEC sites. Figure B-1 shows the study site on Sabine Island at USEPA's Gulf Ecology Division (GED).

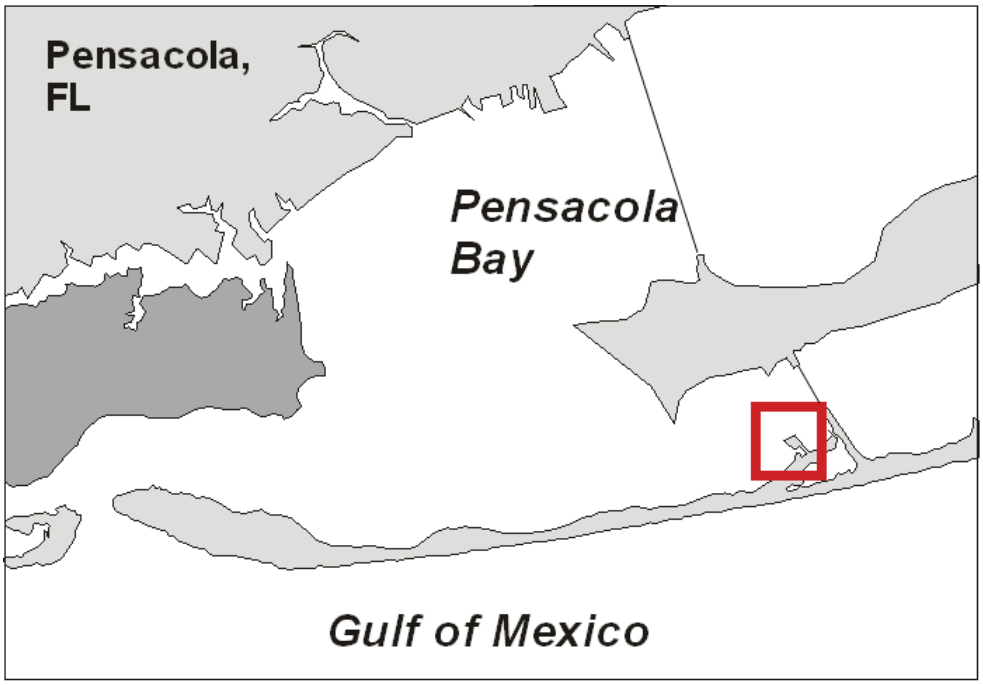

Figure B-1. Study site on Sabine Island at USEPA's Gulf Ecology Division (GED). The study was conducted at the Division's East Dock, located in Santa Rosa Sound, near Pensacola Bay, FL, USA.

B.2 METHODS AND MATERIALS

B.2.1 POCIS AND COMPOSITION B

POCIS samplers and canisters designed for holding three samplers were commercially purchased from Environmental Sampling Technologies, Inc. (St. Joseph, MO, USA). Each sampler has two stainless steel rings that secure two polyethersulfone (PES) membranes with sorbent inside. The exposed membrane surface (41 cm^2 surface area on each side) allows contact to water on both sides of the sampler (Alvarez, 2010). The POCIS, which uses Oasis hydrophilic–lipophilic balance (HLB) sorbent, were deemed appropriate for this study based on recommendations for MC in prior laboratory-based experiments (Belden et al., 2015). A total of 15 g Composition B fragments (individual fragments weighing approximately 200 mg each) was transported from the Naval Air Warfare Center Weapons Center (China Lake, CA, USA) using a commercial carrier, in compliance with U.S. Department of Transportation regulations (permit DOT-SP 13133) and in accordance with U.S. Health and Safety Plan requirements for conducting research with explosives.

B.2.2 FIELD STUDY DESIGN

B.2.2.1 POCIS and Comp B Deployment

Canisters each containing three POCIS were deployed at 19 locations at distances up to 5 m away, both horizontally and vertically forming a concentric circle, from a single "source" canister containing 15 g of Composition B distributed in two 500-µm mesh size stainless steel bags, each approximately 2.5 cm x 10 cm in size (Figures B-2 and B-3). The source canister also contained one POCIS. The POCIS canisters were placed at two different depths, near-bottom (approximately 0.3 m above sea floor) and near-surface (approximately 1.5 m above the sea floor), forming concentric circles to characterize dissolution and transport of MC in the immediate vicinity of the source. The source canister was placed at the center of a 0.6 m x 0.6 m square polyvinyl chloride (PVC) frame,

which maintained the source canister and the inner canisters equidistant from one another (approximately 0.3 m), and was suspended approximately 0.3 m from the sea floor. The middle circle included six canisters at the bottom depth, and four canisters at the surface. The outer circle included four canisters at a mid-water depth (~ 1.5 m) position only. The PVC frame assembly, and all other POCIS canisters, were suspended from the dock by tying off with nylon cord through cross beams supporting the dock below. A single far-field station, approximately 250 m from the source canister on the northwest portion of Sabine Island, served as a reference location where MC was unlikely to be detected.

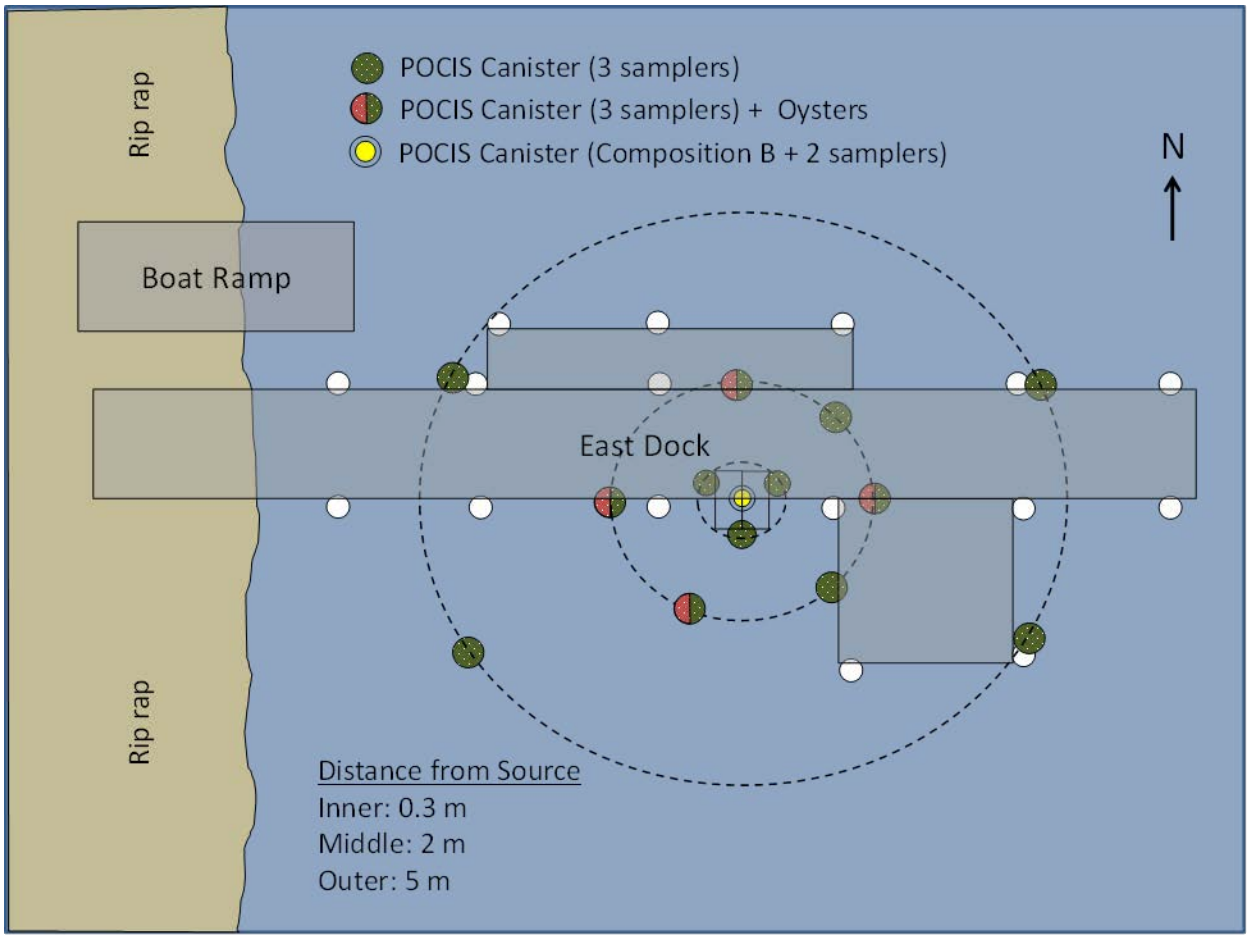

Figure B-2. Top-down view of sampler configuration around source Composition B canister (yellow). Note, some of the 20 canisters deployed not viewable due to being positioned below surface canisters or outside scale (far-field reference canister).

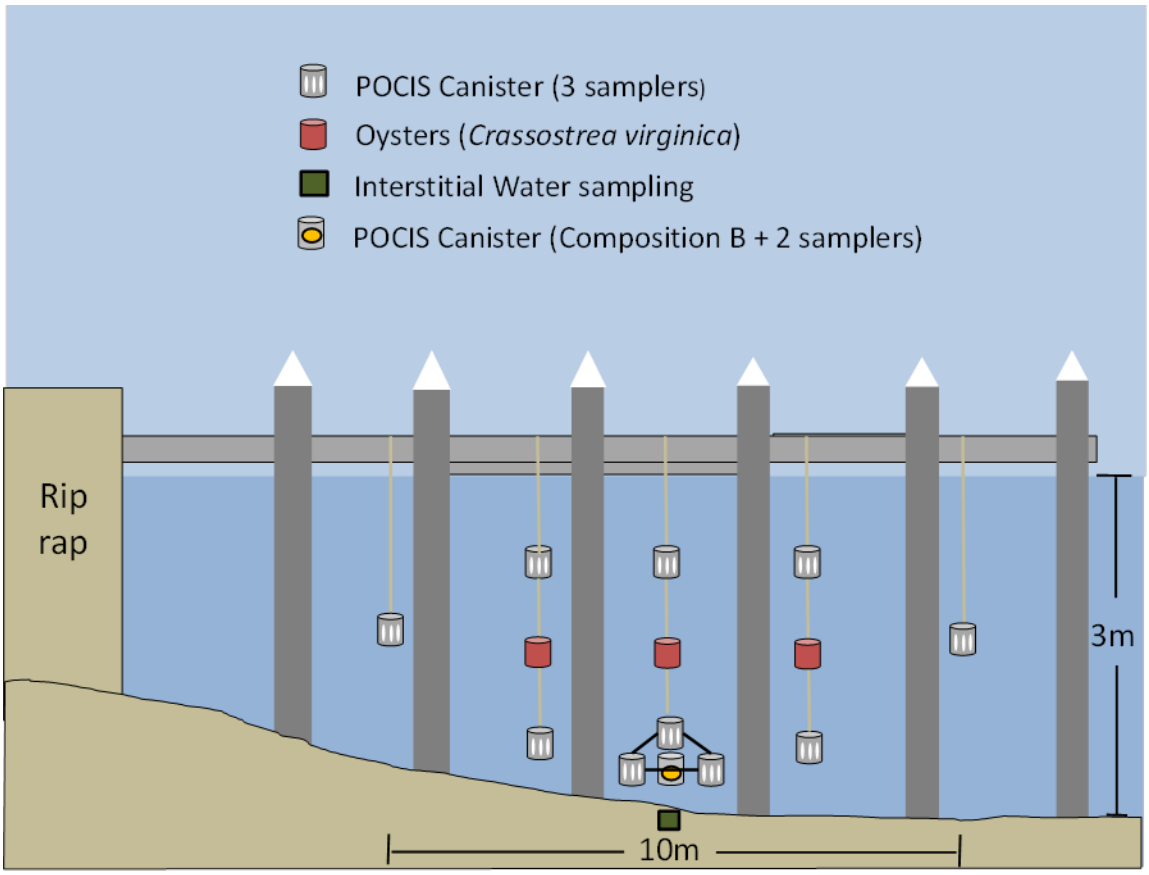

Figure B-3. Simplified cross-section view of placement of POCIS canisters (gray) and oysters (red) around the Composition B source (yellow canister) for 13-day deployment. Sediment cores were removed underneath the canister (green) for interstitial water chemistry. (Note: not all samplers are shown).

B.2.3 DISCRETE WATER SAMPLING

Discrete (grab) water samples (1-L) were collected in duplicate at three time points (days 1, 6, and 13) from the inner ring, within 0.3 m of the source canister. Assuming a continuous pulse of MC dissolving from the source, the average of multiple grab water sample results were considered potentially comparable with estimated TWA concentrations generated using POCIS at the Inner sampling location. For quality assurance and control, three additional 1-L grab samples were collected during the first time point and spiked with a solution containing TNT, RDX, 4-ADNT, and 2-ADNT. The mean recoveries were 73, 128, 96, and 95%, respectively.

B.2.4 OYSTER SAMPLING

For determining potential uptake and bioconcentration into live organisms, caged oysters (Crassostrea virginica) were placed in the vicinity of the POCIS chambers at select locations (Figures B-2 and B-3). The 13-day deployment time was sufficient for MC in water to approach steady-state in bivalves (Rosen and Lotufo, 2007).

Oysters (3” shell length) were shipped overnight from the Bay Shellfish Company (Terra Ceia, Florida) to the GED Toxicology Laboratory, where they were acclimated to site conditions in raw flowing seawater pumped in to the lab from adjacent Santa Rosa Sound (salinity 13 ppt, temperature 21 °C during holding) for 1 week prior to the study. On the deployment day, 10 oysters were

randomly selected for placement into plastic mesh bags (1/2" mesh size), and secured to the nylon rope used to suspend POCIS samplers. Oysters were deployed at mid water depth at six stations (one Central [0.3 m], four Middle [2 m], and one Far-field [250 m]; Figures B-2 and B-3). Ten non-deployed oysters for Time 0 analyses were also frozen on the deployment day.

B.2.5 INTERSTITIAL WATER AND SEDIMENT SAMPLING

Shallow sediment cores (top 10 cm) were collected by snorkel using 2 ¾" inner diameter core liners. Porewater was extracted ex situ shortly after sampling using a syringe method on four intact sediment cores (Nipper et al., 2004). The four sediment samples were subsequently composited and extracted for MC analysis.

B.2.6 DEPLOYMENT TERMINATION

Thirteen days after deployment, final overlying water samples were collected, followed by removal of sampler canisters and oysters from the dock. The POCIS were retrieved and rinsed with deionized water. The oysters were rinsed and shucked. POCIS and oysters were immediately frozen for later analysis. On the recovery day, sediment cores and interstitial water samples were also collected. All samples were shipped on ice with attached chain of custody forms. Data loggers were recovered and data exported to a personal computer.

B.2.7 CHEMICAL ANALYSIS

Analysis of MC in POCIS, water, tissue, and sediment was conducted at Oklahoma State University. Solid-phase extraction (SPE) of sampler extracts and grab samples was performed with Waters Oasis HLB cartridges (6ml/500mg; Waters Corporation, Milford, NH, USA). Analytical standards were obtained from AccuStandard (purity > 99%, New Haven, CT, U.S.A.). ^{13}C- labelled TNT was used as an internal standard (Cambridge Isotope Laboratories, Tewksbury, MA, USA). All solvents and reagents were acquired as ultra-pure or pesticide grade and tested negative for interferences or background contamination of MCs.

Sediment samples (5g) were extracted three times with 20-ml acetonitrile using robust vortexing for 2 min followed by 5 min in a sonication bath. The combined extract was reduced to a final volume of 1 ml. Water samples (0.5 L) were extracted by solid-phase extraction (SPE) on Oasis HLB SPE columns, eluted with ethyl acetate, and brought to a final volume of 0.5 ml using procedures previously described (Belden et al., 2015). POCIS were extracted with ethyl acetate. Tissues were extracted using QuEChERS techniques derived for pesticides, and optimized for TNT, ADNT, and RDX (Anastassiades, and Lehotay, 2003).

The QuEChERS technique involves extraction by acetonitrile followed by cleanup to remove lipids. The initial extraction used is identical to EPA 8330. During the cleanup, a pre-packaged mix of salts was added to the acetonitrile extract to separate water from the solvent. Next, a portion of the solvent was added to a pre-packaged vial containing a mix of sorbents that selectively remove lipids. The extract was then evaporated to 0.1 ml and analyzed.

Extracts were analyzed by GC/MS using GC methods described and optimized by Zhang et al. (2007) and EPA Method 8095 (USEPA, 2007). All extracts were analyzed using an Agilent 6850 GC coupled with a 5975C mass selective detector (MSD) using negative chemical ionization. Negative chemical ionization, which reduces the potential for interferences in field-collected samples, was incorporated by Belden et al. (2015). The following GC/MS configuration was used: GC inlet 190 °C with ultra-inert liners; column- HP-5MS, 15 meters long, 0.25 mm diameter, and 0.25μm film thickness; carrier- 1.2 ml/minute flow helium; 150 °C MS quad; 200 °C MS source; and methane gas as the chemical ionization agent. Internal calibration was performed using ^{13}C-labelled TNT as the

internal standard for all analytes. The quantitation limits for all matrices is shown in Table B-1. Sampling rates and MC mass in the samplers were converted to TWA aqueous concentrations (see Equation 1).

Table B-1. Quantitation limits (QL) for MC in each matrix. Instrumental detection was similar for all matrices. Difference in QL is due to different levels of sample enrichment. *Indicates data are semi-quantiative, as only estimated sampling rates were available, or spiked recoveries were lower suggesting the results are qualitative.

	TNT	RDX	ADNTs	DANTs
3 POCIS (ng)	25	60	25	60
Water column by SPE (ng/L)	50	120	50	120
Water column, 3 POCIS, 13-day (ng/L)	6.1	5.4	6.2-6.6	45*
Tissue (ng/kg)	25000	60000	25000	60000*
Sediment (ng/kg)	10000	24000	10000	24000

B.2.8 WATER QUALITY MEASUREMENTS

Standard water quality parameters including dissolved oxygen, pH, temperature, and salinity were collected using hand-held meters while on site. Onset® HOBO® data loggers (Onset Computer Corporation, Bourne, MA, USA) were deployed at the site for continuous measurement of temperature, conductivity, salinity, and dissolved oxygen in the water column.

B.3 BIOFOULING STUDY

B.3.1 FIELD CONDITIONING OF SAMPLERS

The potential for biofouling of POCIS membranes to affect MC sampling rate was examined in a subsequent deployment at the Santa Rosa Sound site followed by a 7-day laboratory exposure of the fouled POCIS to MC spiked seawater. POCIS canisters were deployed at a water depth of ~ 1m at the mid-section of the research dock for periods of 7, 14, and 28 dau during July 7–August 4, 2015, approximately one year following the MC study. A second 14-day field exposed canister containing three POCIS was immediately frozen for analysis to verify ambient water concentrations at the dock during the fouling study. Timing of deployment was such that all canisters were recovered on the same day (August 4, 2015), followed by immediate transport to the ecotoxicology laboratory at the U.S. Army Corps of Engineers Engineer Research and Development Center in Vicksburg, MS, and initiation of the laboratory experiment on the same day, to minimize degradation of the fouling community. Water quality characteristics of the laboratory study were designed to closely match those observed at the field site (i.e., temperature 22 °C, salinity 23 ppt, pH 8.1, dissolved oxygen >7.0 mg/L).

B.3.2 LABORATORY APPROACH

After careful removal of extraneous fouling on the stainless steel rings to maintain water quality, one of each of the three POCIS for each field exposure period was placed on a wire dish rack in 20 gallon aquaria filled with MC spiked synthetic seawater (reverse osmosis water and Crystal Sea Marinemix™ Bioassay Formula) made to the site salinity and temperature. The MC spike targeted a

1-µg/L water concentration of TNT, RDX, and 2,4-dinitrotoluene (2,4-DNT). Water was renewed three times (days 0, 2, and 4) during the experiment by transferring POCIS to identical freshly spiked tanks. Water samples were collected for chemical analysis on all fresh spiked solutions and on the pre-renewal water for verification of exposure concentrations, for a total of six samples per tank. A set of three unexposed POCIS were analyzed as field blanks. Sampling and chemical analysis of POCIS and water were conducted as described above for the Comp B source study.

B.3.3 MEMBRANE MASS AS ESTIMATE OF RELATIVE FOULING

Following the laboratory study 7-day, the membranes were cut from the stainless steel POCIS rings using a solvent rinsed scalpel. The HLB media was recovered by rinsing into an empty SPE cartridge using deionized water for residue analysis. Membranes were placed in pre-weighed aluminum pans and baked over night at 45 °C to achieve a consistent moisture content. Samples were allowed to cool to room temperature before taking final dry weight measurements of the two membranes associated with each sampler.

B.4 DATA ANALYSIS

POCIS-derived time-averaged water concentrations (C_w) for the field site were calculated using Equation (1):

$$C_w = \frac{N}{R_s t}, \quad (1)$$

where N is the amount of the chemical accumulated by the sampler (ng), R_s is the sampling rate (L/d), and t is the exposure time (d). Sampling rates were calculated for MC in laboratory calibration experiments for ADNTs and DANTs (Belden et al., 2015), while TNT, 2,4-DNT, and RDX sampling rates were selected from Rosen et al., (2017,Guidance Doc) for <7 or 9 cm/s flow conditions, respectively. Although flow was not measured continuously during this study, prior flow conditions were previously documented to average 2.8 cm/s under the east dock, and where available, it is advised that flow corrected sampling rates be used, as flow related artifacts can account for as much as a two-fold error in the calculation of water sampling rate by POCIS (Harman et al., 2012, Lotufo et al., in prep). Sampling rates selected, therefore, were 105, 63, 284, 63, 104, 97, and 34 ml/d, for TNT, 2,4-DNT, RDX, 4ADNT, 2ADNT, and DANTs, respectively. Where appropriate, means, standard deviations, and coefficient of variation were calculated for comparison of variability between or among treatments.

B.5 RESULTS AND DISCUSSION

B.5.1 POCIS-DERIVED MC CONCENTRATIONS IN WATER

Estimated TWA water concentrations for TNT and RDX decreased with increasing distance from the source canister (Table B-1, Figure B-4). The POCIS-derived TWA concentrations for TNT and RDX in the inner ring bottom plane (0.3 m from the source canister) ranged from 46–103 ng/L; Table B-1, Figure B-4). RDX concentrations were lower than those for TNT, even though Composition B is 59.5% RDX/39.5% TNT/1% wax (Lynch et al., 2002). At the middle ring (2 m away from source), POCIS-derived water concentrations from bottom samplers were lower than the inner ring, ranging from 17 to 63 ng/L (Table B-1). All samplers at the outer stations (5 m from source) were below the quantitation limits for POCIS (Table B-2). The concentrations of the primary TNT breakdown products, 2-ADNT and 4-ADNT, were below quantitation limits in the POCIS for

all non-source compartment sampling locations and, therefore, TWA concentrations for those compounds were below QLs.

The POCIS TWA concentrations measured following a 13-day deployment was sufficient to verify that the samplers can reliably detect TNT and RDX at ultra-trace (< 50 ng/L) levels in a field aquatic environment.

B.5.2 SOURCE CANISTER WATER CONCENTRATION

MC concentrations inside the source canister were two orders of magnitude greater than those measured in the Inner Ring, 0.3 m outside of the source canister (Table B-2). In addition to TNT and RDX measured both inside and outside the canister, TWA concentrations were quantified for ADNTs inside the source canister volume only, while DANTs were not detected in any case (outside or inside, regardless of distance). Both 2-ADNT and 4-ADNT, common degradation products of TNT, were two orders of magnitude lower than the parent TNT compound, and likely formed during rapid microbial degradation that is well documented for TNT (e.g., Elovitz and Weber, 1999; Rosen and Lotufo, 2005; Lotufo et al., 2017). In our estimation, the source canister served as a surrogate for the inside cavity of a munition, where MC potentially present at high concentrations inside the cavity is released through one or more breaches. Once released into the environment, the MC are subject to fate processes, such as phase partitioning, microbially driven biodegradation, and transport (e.g., advection, diffusion) processes that exchange the materials between the water column and the resuspended sediment bed. In open water environments, MC dissolve and are released to the overlying water to be carried away from the source by currents, readily diluted, and subjected to similar transformative processes in the water column. Overall, MC persistence in the environment is a key determinant of exposure (Lotufo et al., 2017).

B.5.3 GRAB WATER, TISSUE, AND SEDIMENT MC CONCENTRATIONS

B.5.3.1 Grab Water Samples

Grab water samples collected adjacent to the Composition B source canister resulted in non-detectable concentrations for all analytes (Table B-1). This finding demonstrates one line of evidence of the higher value of POCIS over traditional means of water sampling (e.g., grab sampling) for trace level contaminants.

B.5.3.2 Oysters

Oyster survival was high, averaging 95 ±5% across all stations. Tissue concentrations were below the associated QL (< 25–60 µg/kg; Table B-1) in all samples, including both far-field (reference) and samplers deployed near the source. These findings are corroborated based on the low water concentrations, and low bioconcentration factors (BCF) for other bivalves previously reported for these compounds (Rosen, and Lotufo, 2007; Lotufo et al., 2013, and references therein). The BCF values (1.61 for TNT and 0.87 for RDX) for the Mediterranean mussel (*Mytilus galloprovincialis*) predicted predicted tissue concentrations are 166 and 84 ng/kg, which are 151 and 712 times lower than the QL for tissues, respectively. Put differently, the concentration in the water would need to be above 16 and 69 µg/L for TNT and RDX for the method to detect MC in the oysters, well below that capable of passive samplers. Figure B-4 shows the estimated MC water concentrations from the three distance groupings from the Composition B source canister.

Table B-2. POCIS-derived estimated MC water concentrations at locations up to 5 m from Composition B source.

Station Location Descriptors								Mass per POCIS (ng)				Estimated water concentration (ng/L)			
Sample	Type[1]	Ring	Depth[2]	Direction from source[3]	Horizontal dist. from source (m)	Vertical dist. from source (m)	Total dist. from source (m)[4]	TNT	RDX	4-ADNT	2-ADNT	TNT	RDX	4-ADNT	2-ADNT
1	1	Source	Near Botom	NA	0	0	0	17,800	9,650	135	110	13,040	2,614	100	87
2	2	Central	Near Bottom	North	0.3	0	0.3	109	170	-	-	80	46	-	-
3	2	Central	Near Bottom	Southwest	0.3	0	0.3	141	357	-	-	103	97	-	-
4	2	Central	Near Bottom	Southeast	0.3	0	0.3	113	280	-	-	83	76	-	-
5	2	Central	Near Surface	Center	0	1.8	1.8	13	34	-	-	9	9	-	-
6	2	Middle	Near Bottom	North	2.0	0	2.0	87	100	-	-	63	27	-	-
7	2	Middle	Near Bottom	Northeast	2.0	0	2.0	49	95	-	-	36	26	-	-
8	2	Middle	Near Bottom	East	2.0	0	2.0	26	63	-	-	19	17	-	-
9	2	Middle	Near Bottom	South	2.0	0	2.0	50	76	-	-	37	21	-	-
10	2	Middle	Near Bottom	Southwest	2.0	0	2.0	71	96	-	-	52	26	-	-
11	2	Middle	Near Bottom	West	2.0	0	2.0	39	64	-	-	28	17	-	-
12	2	Middle	Near Surface	North	2.0	1.8	2.7	64	56	-	-	47	15	-	-
13	2	Middle	Near Surface	East	2.0	1.8	2.7	-	-	-	-	-	-	-	-
14	2	Middle	Near Surface	South	2.0	1.8	2.7	-	-	-	-	-	-	-	-
15	2	Middle	Near Surface	West	2.0	1.8	2.7	-	-	-	-	-	-	-	-
16	2	Outer	Mid-depth	Northeast	5.0	1	5.1	-	-	-	-	-	-	-	-
17	2	Outer	Mid-depth	Southeast	5.0	1	5.1	-	-	-	-	-	-	-	-
18	2	Outer	Mid-depth	Southwest	5.0	1	5.1	-	-	-	-	-	-	-	-
19	2	Outer	Mid-depth	Northwest	5.0	1	5.1	-	-	-	-	-	-	-	-
20	3	NA	Mid-depth	NA	~250	1	NA	-	-	-	-	-	-	-	-

[1]Type 1= Inside source canister, Type 2= Outside source canister, Type 3= Far-field reference canister.

[2]Near surface= ~0.75 m below water surface, Near Bottom= ~2.5 m, and Mid-Depth= ~1.5 m. Tidal variation averaged 0.38 (± 0.15) m during study.

[3]Direction in relation to source canister.

[4]Calculated as hypotenuse of horizontal and vertical distance.

Dashes indicated below method detection limits.

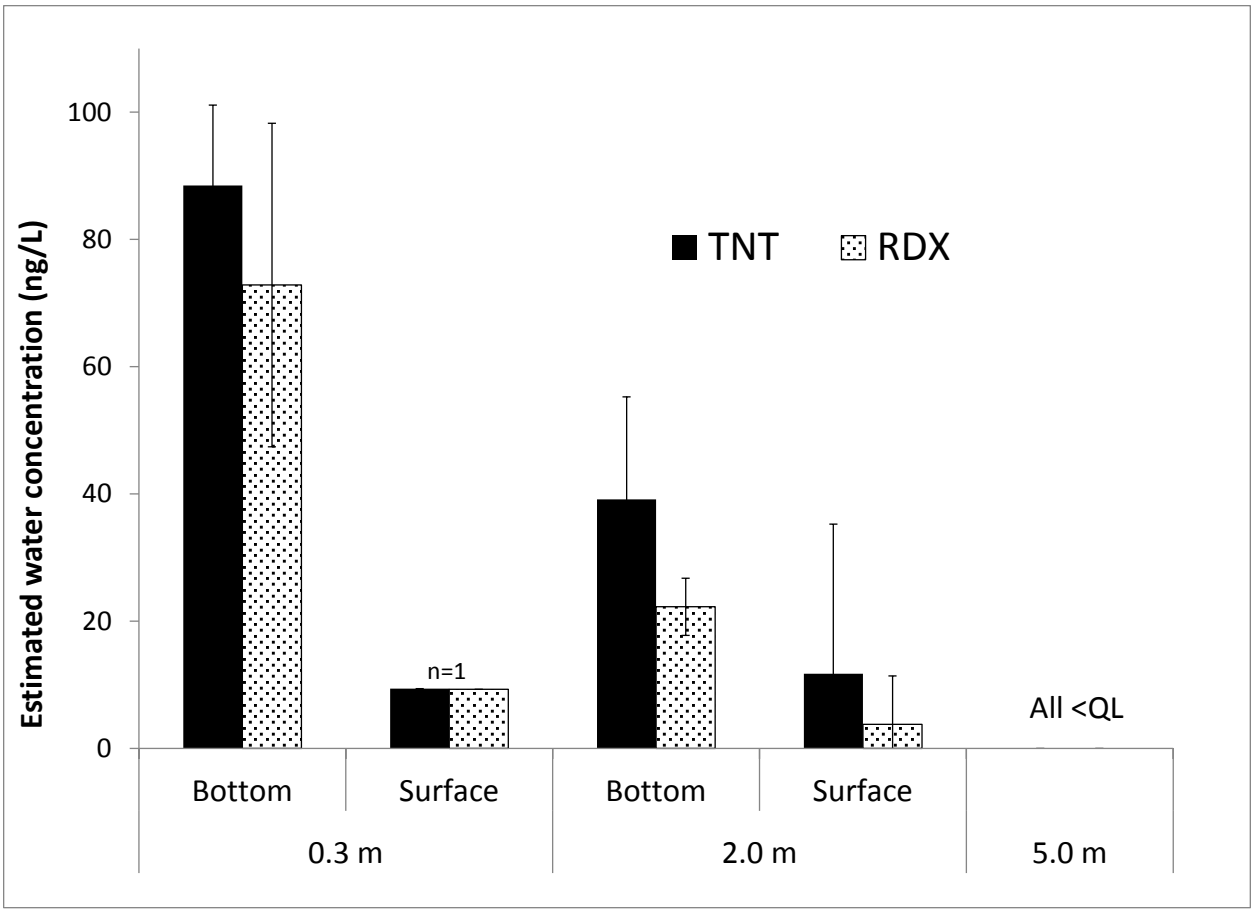

Figure B-4. Estimated MC water concentrations from the three distance groupings from the Composition B source canister. Error bars represent one standard deviation from mean, with N = 3 for 0.3 m Bottom, 1 for 0.3 m Surface, 6 for 2.0 m Bottom, 2 for 0.3 m Surface, and 4 for 5.0 m.

B.5.3.3 Porewater

A single porewater sample was created by compositing water collected using a syringe and air stone (Nipper, Qian, Carr, and Miller, 2004) from four sediment cores (top 10 cm) collected as closely beneath the source canister as possible, representing a worst case exposure scenario. Porewater concentrations for TNT, 2-ADNT, and 4-ADNT ranged from 790 to 950 ng/L, and was 2,100 ng/L for RDX. The presence of ADNTs in sediments contaminated with Composition B is commonly associated with microbial transformation of TNT (Elovitz and Weber 1999; Rosen and Lotufo, 2005). The relatively high RDX concentration may be due to the fact that TNT and its degradation products have a higher affinity for sediment, and may not be less likely to be present in the water phase.

B.5.3.4 Composition B loss

Of the 15 g Comp B that was deployed, dried fragments weighing a total of 13.465 g (representing a loss of 1.535 g) were recovered following the 13-day deployment. The 11.4% mass loss over the 13-day period was similar to the 16% mass lost over a 34-day mesocosm exposure using Composition B fragments placed on the sediment surface (Rosen and Lotufo, 2010).

B.5.3.5 Water Quality

Discrete water quality measurements were made with hand-held calibrated instruments during deployment and recovery. Salinity at the surface (< 1 m depth) and bottom (2.5 m) averaged 5.7 ±1.5 (SD) and 6.8 ±1.9 ‰ during the 13-day deployment. Dissolved oxygen averaged 7.4 ±0.6 mg/L at both the surface and bottom. Temperature averaged 23.9 ±1.8 and 24.2 ±1.9 °C at the surface and bottom, respectively.

Salinity was lower than anticipated at the site based on historical information provided from the GED (Peggy Harris, personal communication), but unprecedented high rainfall (including 20" of rain April 29–30, 2014) during the deployment period, and relatively low circulation at the site likely contributed to the sustained low levels during the exposure period.

B.6 BIOFOULING IMPACTS ON MC UPTAKE BY POCIS

B.6.1 BIFOULING

Biofouling from the 0–28 day conditioning period at the Santa Rosa Sound site prior to laboratory exposure in spiked aquaria was evaluated visually (qualitatively) and quantified as total fouling mass on the membranes. A visual comparison of representative membranes indicates light fouling through day 14, followed by heavier fouling by day 28 (Figure B-5). Significantly greater mass of fouling organisms was observed for the 28–day samplers only, in comparison to unexposed (0 day) samplers (one-way ANOVA with pairwise comparisons, $p = 0.014$).

B.6.2 MC IN THE EXPOSURE WATER

A total of six water samples were collected from each of the three study tanks for chemical analysis during the 7-day exposure; three measurements associated with the fresh spikes (days 0, 2, and 4) and three measurements associated with the aged/exposed time points (days 2, 4, and 7). For freshly spiked water, the measured concentrations were on average, 107, 106, and 138% of the target concentration for 2,4-DNT, TNT, and RDX, respectively (Table B-3). Prior to renewals, concentrations were, on average, 78, 40, and 147% of the target concentration, respectively (Table B-3). Lower concentrations following 2–3 days post-spike for TNT and 2,4-DNT, are likely associated with the rapid transformation of those nitroaromatic compounds to daughter products in presence of biota associated with the fouling in each tank, as observed previously in bioassay exposure water, especially with the presence of supplemental food (Lotufo, Blackburn, and Gibson, 2010), and removal by the POCIS. RDX tends to be more resistant to biotic degradation in the presence of bioassay organisms (Lotufo et al., 2010). Figure B-6 shows the Mean (± s.d.) membrane dry weight (mg) from POCIS samplers (N = 3) following 0 to 28 days of exposure at Gulf Breeze east dock. Figure B-7 shows an example laboratory tank showing one replicate from each field exposed time point.

Figure B-5. Representative pictures of POCIS membranes upon initiation of 7-day MC spike laboratory experiment following deployment at Gulf Breeze East Dock (from left to right), for 0, 7, 14, and 28 days during July 7–August 4, 2015.

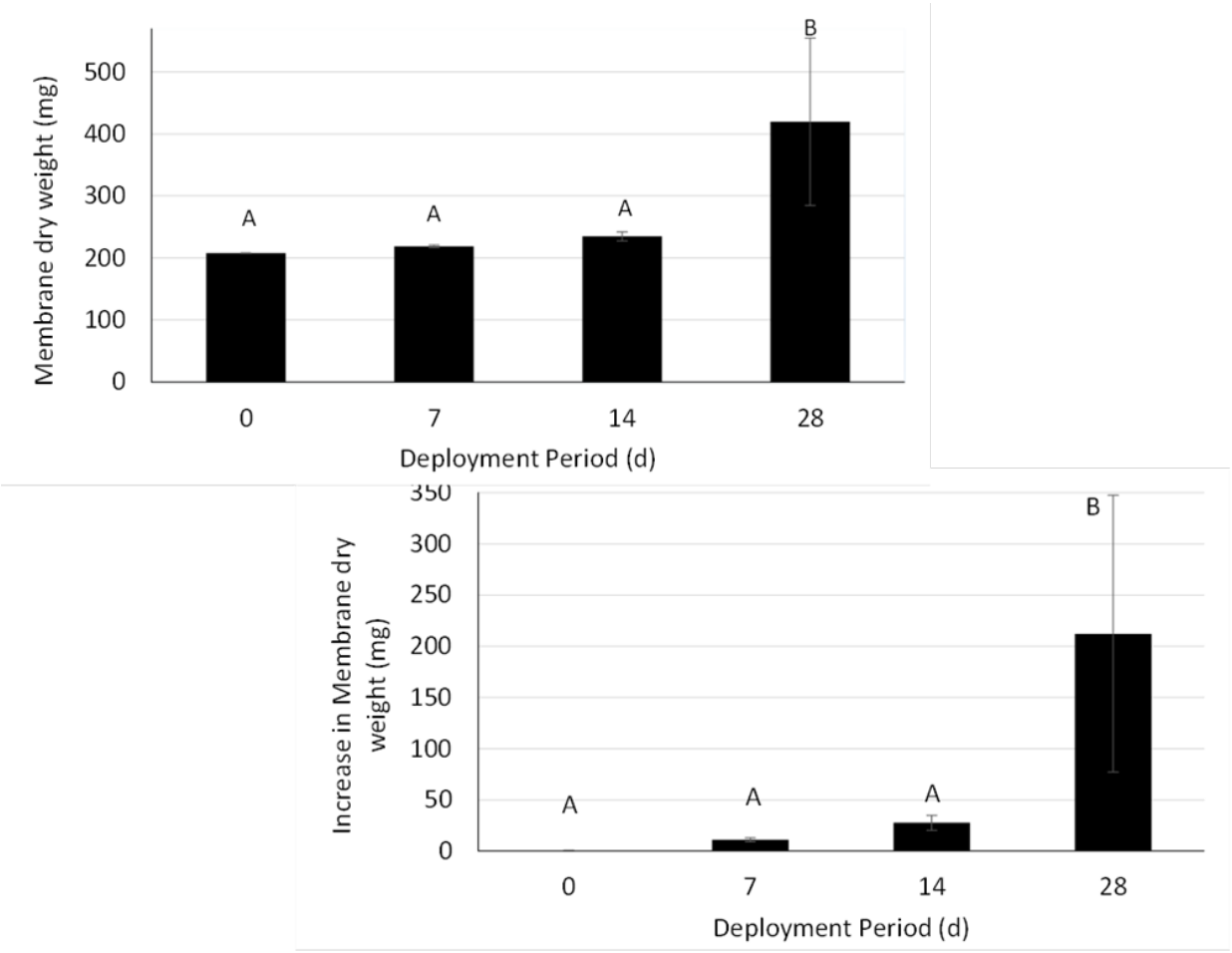

Figure B-6. Mean (± s.d.) membrane dry weight (mg) from POCIS samplers (N = 3) following 0 to 28 days of exposure at Gulf Breeze east dock (July 7-August 4, 2015), following the 7-day spiked MC study with samplers in the laboratory. Different letters indicate significant differences from pairwise comparisons with Tukey-Kramer test (α = 0.05). Membrane weights for all samplers (top) and in comparison to non-field exposed sampler (bottom).

Figure B-7. Example laboratory tank showing one replicate from each field exposed time point (0 to 28 day) for POCIS prior to placement in lab exposure with nominal 1 µg/L 2,4-DNT, 2,4,6-TNT, and RDX in reconstituted seawater.

Table B-3. Measured spiked MC concentrations in tanks for biofouling study, including those before and after water renewal.

	N		2,4DNT	TNT ng/L	RDX
Mean	6	Tank 1	854 (196)	680 (369)	1472 (366)
Mean	6	Tank 2	956 (176)	727 (388)	1281 (364)
Mean	6	Tank 3	952 (213)	774 (355)	1521 (649)
Mean	18	All Tanks	920 (57.3)	727 (46.9)	1425(127)
CV	18	All Tanks	6.2	6.5	8.9
Fresh Spikes only	9	All Tanks	1066 (139)	1055 (399)	1378 (253)
Prior to Renewal	9	All Tanks	775 (97.1)	399 (117)	1472 (621)

B.6.3 MC UPTAKE IN FOULED POCIS

Mass of MC in POCIS for each of the fouling conditions following a 7-day spiked exposure are shown in Figure B-8. Mean uptake of 2,4-DNT was about a factor of two less than TNT, and an order of magnitude lower compared to RDX. Mass per POCIS for 2,4-DNT, TNT, and RDX were roughly in line with their sampling rates under relatively static conditions (63, 105, and 284 ml/d, respectively; ESTCP ER-201433 Guidance Document). For TNT and RDX, there was no statistical difference between non-field exposed (day 0) and any fouled POCIS, including 28-day field exposed

samplers. For 2,4-DNT, all fouled samplers resulted in statistically lower uptake than the non-field exposed POCIS. However, there was no increase in the uptake with increasing fouling (i.e., among 7, 14, and 28-day pre-exposed samplers), with means differing by less than 10%, and the 28-day fouled samplers only lower than non-field exposed samplers by 26%. Table B-4 shows Mass (means and standard deviations) of MC accumulated on POCIS samplers in 7-day spiked laboratory exposures following field deployment of samplers at Santa Rosa Sound, FL, for 0 to 28 days.

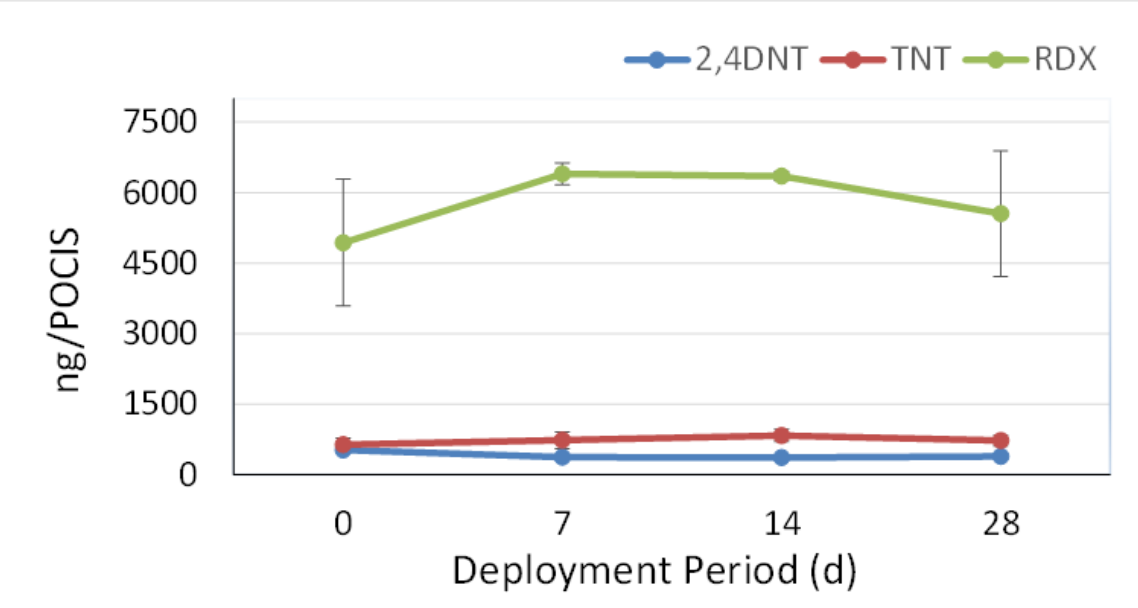

Figure B-8. Mass (means and standard deviations) of MC accumulated on POCIS samplers in 7-day spiked laboratory exposures following field deployment of samplers at Santa Rosa Sound, FL, for 0 to 28 days.

Table B-4. Mass (means and standard deviations) of MC accumulated on POCIS samplers in 7-day spiked laboratory exposures following field deployment of samplers at Santa Rosa Sound, FL, for 0 to 28 days.

Days Field Exposed	2,4DNT	TNT ng/POCIS	RDX
0	529 (62.0)	642 (133)	4935 (1350)
7	376 (44.1)	733 (181)	6396 (234)
14	366 (49.6)	835 (134)	6353 (88.2)
28	392 (30.4)	726 (116)	5553 (1335)

B.7 CONCLUSIONS

This field study demonstrates the utility of using HLB POCIS as a cost-effective, sensitive, and relatively simple means of quantifying munitions constituents (MC) exposure concentrations in underwater environments in a time-integrative approach. Our results expand upon previous laboratory-based experiments that demonstrated POCIS-derived TWA concentrations are in good agreement between time-averaged MC concentrations from repeated sampling of water and those generated using POCIS deployment in laboratory experiments (Belden et al., 2015). The use here of Composition B in a POCIS canister simulates release of explosive fill material inside a breached shell to the water column or sediment-water interface. The low (~ 100 ng/L or less) average water concentrations measured within 0.3 m of the source were expected considering the mass (15 g) of explosive used and slow dissolution rate of constituents within Composition B exposed to water (Lynch et al., 2002), which resulted on the release of only 1.5 g sum mass of TNT and RDX . The concentration varied over both horizontal and vertical distances from the source, due to dilution, with highest TNT and RDX concentrations less than 0.3 m from the source, and rapid reduction to non-detectable levels at the 5-m sampling locations. The highest concentrations measured 0.3 m away from the source canister are several orders of magnitude lower than those that are known to be toxic to environmental receptors (Nipper, Carr, and Lotuufo, 2009; Lotufo, Rosen, Wild, and Carton, 2013). Further, the lack of quantitative identification of MC in sediment, tissue, and grab water samples suggests that POCIS was the most sensitive and informative measure of exposure. Therefore, we believe that POCIS can increase certainty with respect to environmental exposure and assist with environmental management decisions at underwater military munitions sites. Furthermore, POCIS can be used to cost-effectively identify individual munitions within sites that might be point sources of MC contamination to the environment.

APPENDIX B
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APPENDIX B
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APPENDIX C
SPIKED FLUME STUDY RESULTS

INVESTIGATION OF POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS) FLOW RATE DEPENDENCE FOR MUNITIONS CONSTITUENTS IN UNDERWATER ENVIRONMENTS

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ABSTRACT

Munitions constituents (MC) are present in aquatic environments throughout the world. Potential for fluctuating release with low residence times may cause concentrations of MC to be vary widely over time at contaminated sites. Recently, polar organic chemical integrative samplers (POCIS), have been demonstrated to be valuable tools for the environmental exposure assessment of MC in water. Flow rate (R_s) is known to influence sampling by POCIS. Because POCIS R_s for MC have only been determined under quasi-static conditions, the present study evaluated the uptake of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and of 2,4- and 2,6-dinitrotoluenes (DNT) by POCIS in a controlled water flume at 7, 15, and 30 cm/s in 10-day experiments using samplers both within and without protective canisters. R_s increased linearly with flow rate for all MC investigated, but flow rate had the strongest impact on TNT and the weakest impact on RDX. For uncaged POCIS, sampling rates at 30 cm/s exceeded those at 7 cm by 2.7, 1.9, 1.9 and 1.3 fold for TNT, 2,4-DNT, 2,6-DNT and RDX, respectively. For all MC except RDX, R_s for caged POCIS at 7 cm/s were significantly lower than for uncaged samplers and similar to those measured at quasi-static condition, but no caging effect was measured at 30 cm/s, indicating that protective canisters mitigate the impact of flow on MC uptake at low flow. Linear regressions were developed for the selection of the most accurate R_s when determining TWA concentrations generated by POCIS deployed at sites contaminated with MC when flow rates are known.

Keywords Passive sampling, POCIS, laboratory calibration, flume, TNT, RDX

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C.1 INTRODUCTION

Manufacturing of munitions constituents (MC), their loading, assembling and packing into munitions, and their use in testing, training, and combat has resulted in their release into terrestrial and aquatic systems (Monteil-Rivera et al., 2009; Juhasz and Naidu, 2007; Amaral et al., 2016). In addition, until 1970, it was accepted practice to dispose of wastes, including excess, obsolete and unserviceable munitions, in deepwater areas (Carton and Jagusiewicz, 2009). As a result, thousands of sites in the USA and throughout the world are potentially contaminated with MC in soil, sediment, groundwater and surface water of inland and coastal habitats (Talmage et al., 1999; Sunahara, Lotufo, Kuperman, and Hawari, 2009; USEPA, 2014a, 2014b). Many active and former military installations have ranges and training areas that include aquatic environments, such as ponds, lakes, rivers, estuaries and coastal ocean areas.

A number of challenges prevent accurate assessment of environmental exposure to MC using traditional sampling approaches (Rosen et al., 2016). Due to the short-half life, and potential for fluctuating release with low residence times, concentrations of MC are likely to be variable at contaminated sites. Standard environmental sampling, such as grab sampling of surface water or collection of sediment, may inadequately capture pulsed concentrations that may occur, thereby not providing an environmentally relevant measure of dose. Similarly, passive sampling devices using an equilibrium approach will likely inaccurately describe a pulse of material as the system is not in equilibrium. For example, if the sample is collected during low environmental concentrations, estimated water concentrations would be biased low. In contrast, integrative passive sampling provides an opportunity to sample MC and obtain time-weighted water concentrations and very low detection limits in water (Belden et al., 2015; Rosen et al., 2016). Commercially available POCIS have effectively linear uptake for at least 28 days for many MC and are highly integrative (Belden et al., 2015).

Integrative samplers predict in situ time-weighted water concentrations using sampling rates determined by deploying samplers for a prescribed period of time to known concentrations in the water, as recommended in Morin, Miege, Randon, and Coquery (2012) and Harman, Allan, and Vermeirssen (2012). Sampling rates are typically empirically derived during laboratory studies employing a closed system in which the contaminants are spiked only at the beginning of the experiment or at constant time intervals (e.g., Mazzella, Dubernet, and Delmas, 2007; Arditsoglou, and Voutsa, 2008). Sampling rates have also been determined in in the field (Jacquet et al., 2012; Mazzella et al., 2010), but it is costly and time consuming. Because environmental conditions such as flow rate, orientation of the POCIS relative to flow, salinity, temperature, and biofouling have potential to cause variations in the sampling rate (Söderström, Lindberg, and Fick, 2009; Harman, Allan, and Vermeirssen, 2012; Lissalde, Mazzella, and Mazellier, 2014), sampling rates should be derived under conditions that reasonably match those for the site of deployment. The potential bias for temperature and salinity is typically low as long as calibration studies are conducted under conditions similar to expected field conditions, and previous work (Harman, Boyum, Tomas, and Grung, 2009; Lissalde, Mazzella, and Mazellier, 2014) has demonstrated little effect of biofouling on sampling rate.

The potential for flow rate to influence sampling has been previously investigated (Li, Vermeirssen, Helm, and Metcalf, 2010; Charlestra et al., 2012; Di Carro, Bono, and Magi, 2013; reviewed in Harman et al., 2012) and generally indicated that increasing flow rate cause increases in sampling rate by less than two-fold. Although most studies indicate that the use of sampling rates derived from simple calibration studies are generally adequate for obtaining a fairly accurate estimate

of TWA concentrations of contaminants using POCIS, uncertainty remains regarding the influence of flow rate on the uptake of MC by POCIS because sampling rates for MC have only been determined under quasi-static conditions (Belden et al., 2015).

The primary objective of this study was to evaluate MC uptake by POCIS in a controlled water flume with known varied current velocities. In addition to investigating the influence of flow rate on sampling rate, we also investigated the influence of location in the flume, orientation of the POCIS relative to the flow and of the presence of the protective canister on sampling rate. We expected this effort to allow for more accurate quantitation of trace level energetics in the vicinity of potentially leaking underwater munitions at UWMM sites.

C.2 MATERIAL AND METHODS

C.2.1 PASSIVE SAMPLERS AND CHEMICALS

POCIS filled with Oasis® hydrophilic–lipophilic balance (HLB) sorbent and stainless steel POCIS holders and protective canisters (Alvarez et al., 2004) were obtained from Environmental Sampling Technologies (St. Joseph, MO, U.S.A.). The dinitrotoluene isomers (2,4-DNT and 2,6-DNT) were purchased from ChemService (West Chester, PA). The aminodinitrotoluene isomers (2-ADNT and 4-ADNT) were purchased from Stanford Research Institute (Menlo Park, CA). Military-grade TNT (contains ≤ 1% other TNT isomers and DNTs) and RDX (contains ≤ 10% HMX) flakes were obtained from the Holston Army Ammunition Plant (Kingsport, TN, USA).

C.2.2 FLUME

Experiments were conducted in the Cognitive Ecology and Ecohydraulics Flume (CEERF) located at the Engineer Research and Development Center in Vicksburg (MS, USA). The CEERF is an annular recirculation flume with two functional domains, each 2.4 m wide, 1.2 m deep (water depth), 12.2 m long (Figure C-1). The flume has repeatable and stable velocities from near 0 to greater than 30 cm/s. The flume has a rectilinear flow field with minimal turbulence and secondary circulation. Mechanically, chemically and electrically isolated with optional mechanical, carbon and ultraviolet filtration.

C.2.3 DETERMINATION OF SAMPLING RATES UNDER VARYING FLOW RATES

The effects of flow rate on the sampling rate (R_s) of MC were evaluated in three separate experiments each using a different flow rate, namely 7, 15, and 30 cm/s, using a large flume (Figure C-1). POCIS were placed in triplicate at eight locations on one side of the flume, four downstream from the spiking point, and four upstream from it (Figure C-2). Each POCIS was mounted on a custom made base (Figure C-1). All POCIS were oriented parallel to flow, except for three POCIS at location 2 upstream from the spiking point, which were oriented normal to flow (Figure C-2). To compare the effect of caging on R_s, POCIS placed in three protective metal canisters (or cages) (Figure C-1), with three samplers per canister, were placed on the side of the flume opposite to the spiking point. After all samplers were in place, the flume was filled with approximately 62,000 L of dechlorinated and filtered tap water. The target temperature was 25 °C.

After the target temperature and flow rate were achieved, flume water was spiked with TNT, 2,4-DNT, 2,6-DNT and RDX targeting 1 µg/L each. Spiking stocks were created by adding the appropriate mass of the above chemicals to 20 mL of acetone. The acetone stock was mixed with 3 L of flume water in an Erlenmeyer flask and that dosing solution was delivered to the flume at a rate of approximately 6 mL/min via rubber tubbing using a peristaltic pump over a period of approximately 8 hours.

Flume water (1 L) was collected on days 1, 3, 7, and 10 in duplicate for chemical analysis. Approximately 10 days after initiation of spiking and deployment to spiked water under constant flow, POCIS were removed from the partially drained flume, POCIS were stored on dry ice, or frozen (-30 °C) until analysis.

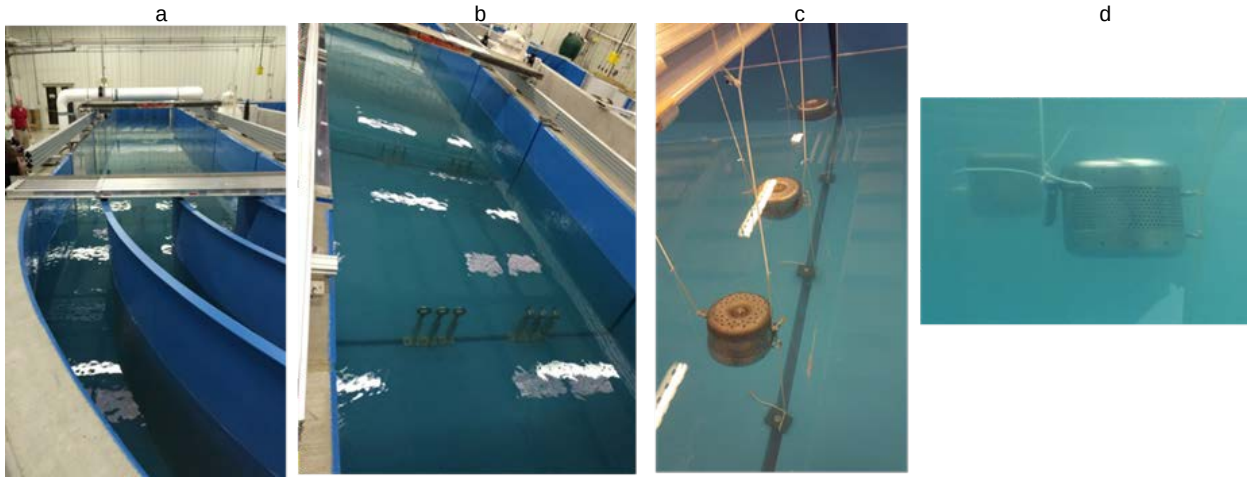

Figure C- 1. From left to right: (a) partial view of the 113,000 L flume; b) POCIS in multiple locations and orientations; (c and d) POCIS deployed inside protective canisters.

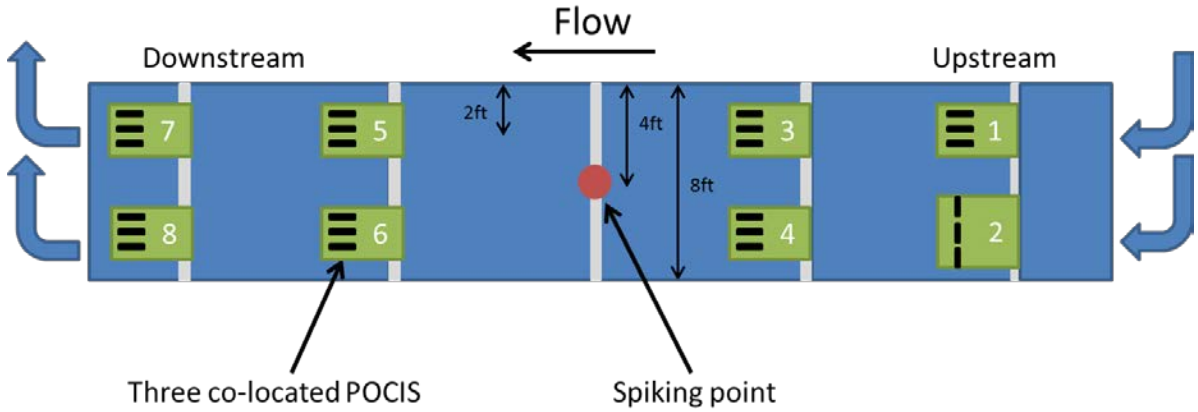

Figure C- 2. Schematic showing the locations of the spiking point and of groups of three POCIS mounted on custom-made bases. POCIS placed inside protective canisters were deployed in triplicate canisters in the opposite side of the flume.

C.2.4 CHEMICAL ANALYSIS

Analysis of MC in POCIS and in water was performed for flow rate calibration. Water samples (1 L) collected on days 1, 3, 7, and 10 were extracted by solid-phase extraction (SPE) on Oasis® HLB SPE cartridges (6 ml/500 mg; Waters Corporation, Milford, NH), eluted with ethyl acetate, and brought to a final volume of 0.5 ml using procedures optimized by Belden et al. (2015).

POCIS were disassembled and the sorbent was rinsed into empty SPE tubes. Sorbent from triplicate samplers from each of the eight locations and from each of the three canisters were composited to maximize detection. MC were eluted with ethyl acetate and brought to a final volume of 0.5 ml. Extracts were analyzed using an Agilent® 6850 GC coupled with a 5975C mass selective

detector (MSD) using negative chemical ionization using 3 ion select ion monitoring for each analyte. Internal calibration was performed using ^{13}C-TNT (Belden et al., 2015).

C.2.5 CALCULATION OF SAMPLING RATES AND OTHER STATISTICS

For compounds in which accumulation was linear over at least part of the 28-day study (Belden et al., 2015), sampling rates (R_S) were calculated for each POCIS based on Equation 1 (Alvarez et al., 2004), rearranged to estimate R_S from known C_w.

$$C_w = \frac{N}{R_s t} \quad (1)$$

where R_S is the sampling rate (L/POCIS/day), N is the mass of the chemical accumulated by the sampler (ng), C_w is the mean measured water concentration (ng/L) and t is the exposure time (days).

The following were evaluated using analysis of variance (ANOVA): (1) the concentration of MC in the water over time, (2) the effect of protective canister on R_S at each flow rate, and (3) the effect of flow rate on R_S for caged and uncaged POCIS. Each MC was analyzed independently. Unless otherwise noted, data are expressed as means ± standard deviations. All statistical calculations were performed using SPSS Software (IBM, New York, NY) and significance was determined at $\alpha = 0.05$.

C.3 RESULTS AND DISCUSSION

C.3.1 CHEMICAL ANALYSIS

Determination of sampling rates were successfully conducted using a closed system in-lab static calibration in which MC were spiked only at the beginning of the experiment (Mazzella, Dubernet, and Delmas, 2007), according to Morin et al. (2012), the most used approach for POCIS calibration. The concentration of MC remained relatively constant between day 1 and termination (Figure C-3), with concentration decreases higher than 20% between sampling times only observed for TNT in the 30 cm/s experiment (between days 3 and 7) and for 2,6-DNT (between days 7 and 10) in the 7 cm/s experiment. Only the 2,6-DNT decrease between days 7 and 10 was statistically significant. The low concentration of 2,6-DNT at day 1 of the 7 cm/s experiment remains unexplained.

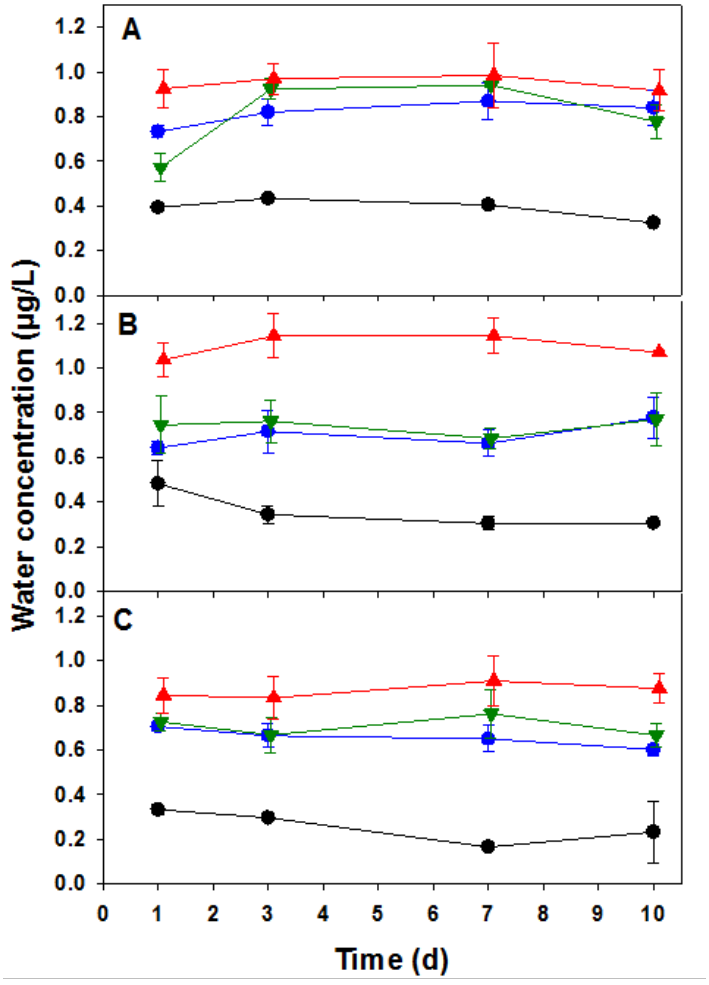

Figure C- 3. Mean concentrations of MC in flume water (collected as grab samples) at each sampling episode during 10 days at 7 cm/s (A), 15 cm/s (B), and 30 cm/s (C). Error bars represent ±1 standard deviation. Black = TNT, blue = 2,4-DNT, green = 2.6-DNT, and red = RDX.

C.3.2 INFLUENCE OF LOCATION, ORIENTATION, AND PROTECTIVE CANISTER ON UPTAKE

For POCIS oriented parallel to flow, differences in sampling rates were typically less than 10% and only exceeded 30% for 9 pairwise comparisons out of 504, suggesting that no substantial effect of POCIS position on the flume. However, orientation of uncaged POCIS relative to flow appeared to have had some influence on sampling rate. Sampling rate for location two POCIS, oriented normal to flow, were consistently lower than for adjacent location one POCIS by an average of 30, 26, 24, and 9% for TNT, 2,4-DNT, 2,6-DNT, and RDX, respectively (Figure C-4). No effect of orientation (parallel and perpendicular to the flow) was previously reported for pesticides uptake by POCIS in natural streams under approximate flow velocity of 4–5 cm/s (Lissalde, Mazzella, and Mazellier, 2014).

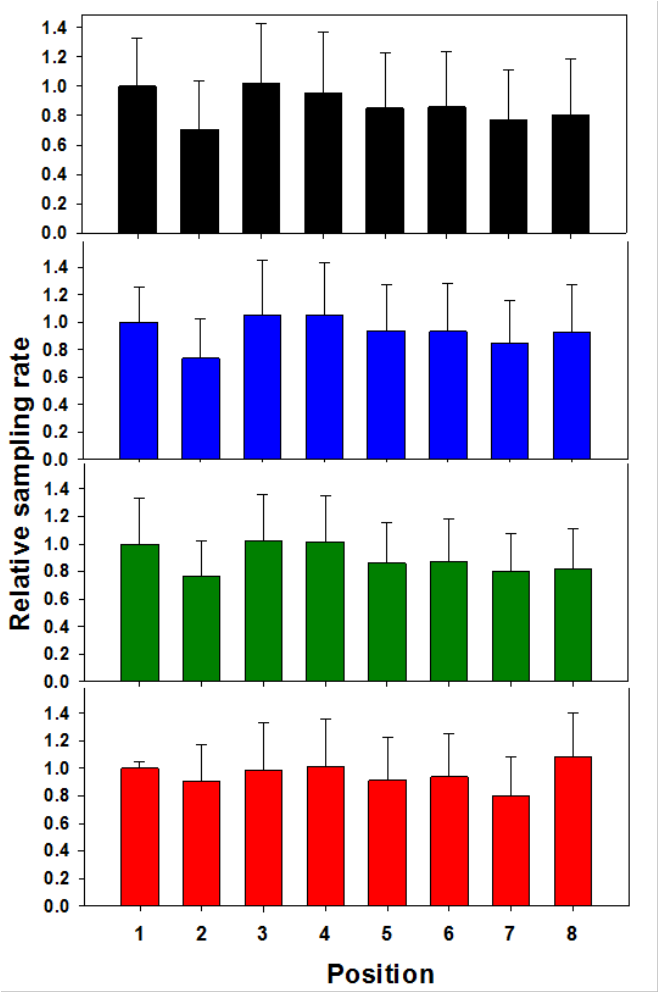

Figure C- 4. Comparison of sampling rates at different locations in the flume. All POCIS were oriented parallel to flow, except for those at location 2, which were oriented normal to flow. To simplify comparisons, sampling rates for location 1 were arbitrarily assigned the value of 1. Error bars represents standard 1 deviation based upon variability across experiments. Black = TNT, blue = 2,4-DNT, green = 2.6-DNT, and red = RDX.

The influence of protective canister on sampling rate (Figure C-5 and Table C-1) was assessed using the eight uncaged POCIS locations three POCIS composite samplers per location) and the three adjacent canisters three POCIS composite samplers per canister) as replicates. At 7 cm/s, sampling rate was significantly lower for POCIS within canisters for all MC except RDX. The decrease in sampling rate with caging observed for most MC evaluated was as expected, according to Cernoch et al. (2011), protective canisters mitigate the impact of flow on chemical uptake. The sampling rate of TNT at 7 cm/s for caged POCIS (0.12 L/d) was similar to that observed under quasi-static conditions (0.09 L/d) for TNT by Belden et al. (2015). However, the caging did not decrease the sampling rate of RDX at 7 cm/s, which were substantially higher than the sampling rate (0.13 L/d) reported by Belden et al. (2015). The effect of caging was overall less dramatic at 15 cm/s, for which only the sampling rate of 2,6-DNT and RDX were significantly decreased. At the highest flow rate studied (30 cm/s), caging did not decrease the sampling rate of any MC investigated, indicating that the mitigating effect of caging on flow decreases with increasing flow rate.

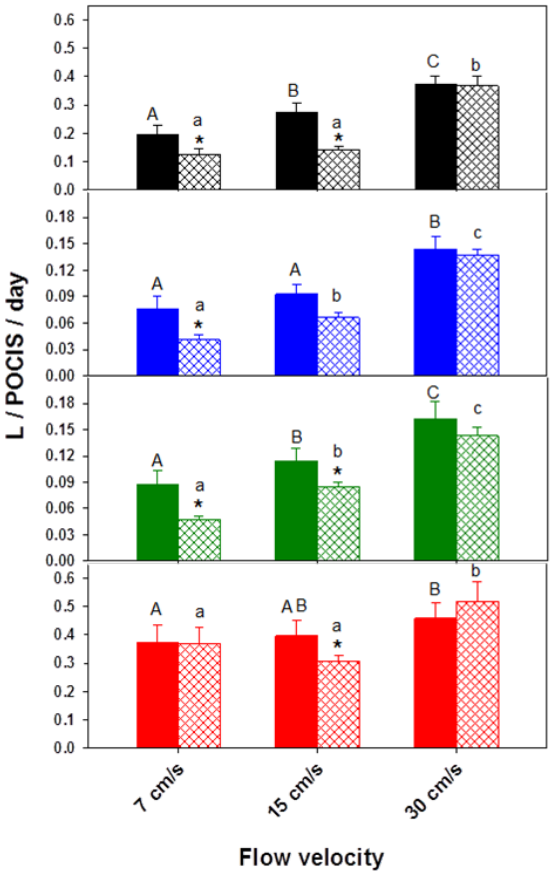

Figure C- 5. Comparison of sampling rates for different flow velocities. Solid and hatched bars represent uncaged and caged POCIS, respectively. Black = TNT, blue = 2,4-DNT, green = 2.6-DNT and red = RDX. Error bars represents one standard deviation. * represent significantly difference between uncaged and caged POCIS, and letters (uppercase and lower case characters are used for uncaged and caged POCIS, respectively), indicate significant differences based on pairwise comparisons (Tukey's test, α = 0.05) following one-way ANOVA.

Table C- 1. Sampling rates for uncaged and caged POCIS measured at different flow velocities and caging configurations. * represent significantly difference.

MC	Sampling rate (L/d)					
	7 cm/s		15 cm/s		30 cm/s	
	Uncaged	Caged	Uncaged	Caged	Uncaged	Caged
TNT	0.20	0.12*	0.28	0.14*	0.52	0.52
2,4-DNT	0.08	0.04*	0.09	0.07	0.14	0.14
2,6-DNT	0.09	0.05*	0.11	0.09*	0.16	0.14
RDX	0.34	0.37	0.40	0.31*	0.46	0.52

C.3.3 INFLUENCE OF FLOW RATE ON SAMPLING RATE

Flow rate had a significant effect ($p < 0.01$) on sampling rate for every MC for both uncaged and caged POCIS. Sampling rates at 30 cm/s were significantly higher than at 7 cm/s for every MC, for both uncaged and caged POCIS (Figure C-6). For uncaged POCIS, sampling rates at 30 cm/s exceeded those at 7 cm by 2.7, 1.9, 1.9 and 1.3 fold for TNT, 2,4-DNT, 2,6-DNT and RDX, respectively, and differences between 15 cm/s and 30 cm/s and between 7 cm/s and 15 cm/s were 1.5 fold or less, except for TNT between 15 cm/s and 30 cm/s (1.9 fold) (Figure C-6). For caged POCIS, sampling rates at 30 cm/s exceeded those at 7 cm by 4.1, 3.4, 3.0 and 1.4 fold for TNT, 2,4-DNT, 2,6-DNT and RDX, respectively, and differences between 15 cm/s and 30 cm/s and between 7 cm/s and 15 cm/s were 2.0 fold or less, except for TNT between 15 cm/s and 30 cm/s (3.6 fold) (Figure C-6).

For the range of flow rates here examined, sampling rate increased linearly for all MC investigated, for both uncaged and caged POCIS, with a strong fit ($r^2 \geq 0.79$) for TNT and DNTs, but with a weaker fit (r^2 0.46 and 0.53) for RDX (Figure C-6 and Table C-2). Based on linear relations, flow rate had the strongest impact on TNT (steepest slope) and the weakest impact on RDX. Flow rates presented in Table C-1 and equations presented in Table C-2 should be used to select the most appropriate sampling rate use in Equation 1 when determining TWA concentrations generated by POCIS deployment at site contaminated with MC when flow rates are known.

The influence of flow rate to influence sampling has been previously reported (reviewed in Harman, Allen, and Vermeirseen, 2012). Only a few studies adequately characterized the influence of properly measured flow rate and sampling rate. Li et al. (2010) found that the POCIS uptake of pharmaceutical, personal care products and endocrine-disrupting compounds varied by less than two-fold for flow rates ranging from 2.6 and 37 cm/s, with sampling rates increasing slightly with flow rates. Charlestra et al. (2012) demonstrated that mixing, either by flowing water or by stirring, increases pesticide uptake by the POCIS, generally by less than two-fold. Using flow rates ranging from 2 to 15.3 cm/s, Di Carro, Bono, and Magi (2013) reported no noticeable influence of flow rates on the sampling rates of contaminants from different chemical classes. Carpinteiro et al. (2016) reported that an increase of water velocity from 2 to 50 cm/s results in an increase of the amount of pharmaceuticals accumulated in the POCIS by factors ranging from 1.4 to 2.3.

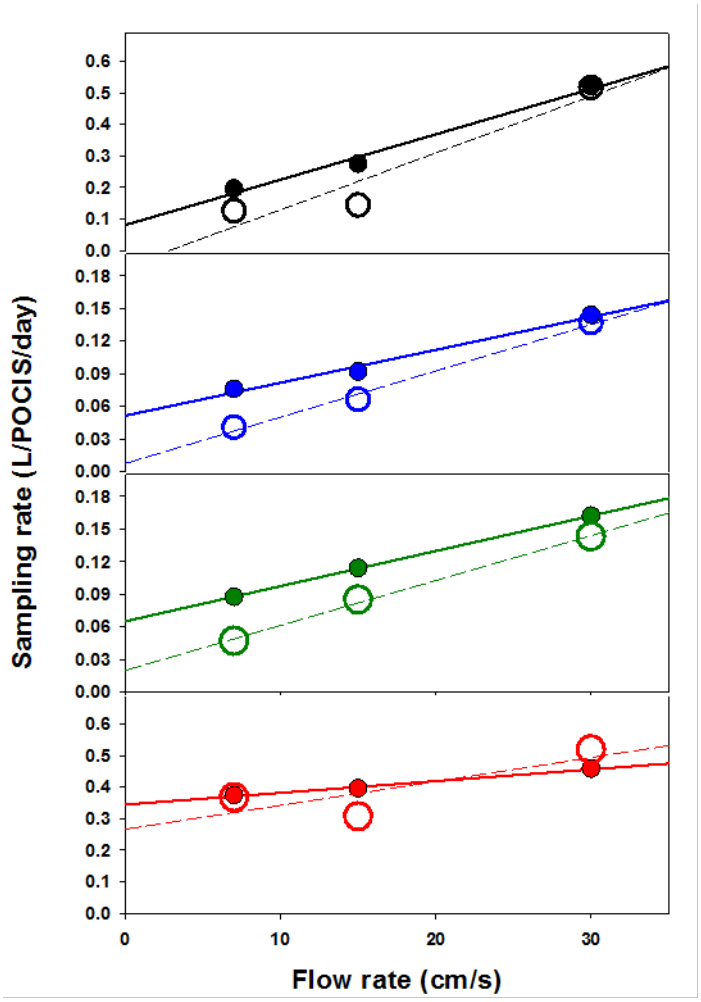

Figure C- 6. Relation between sampling rate and flow rate for uncaged (solid circles) and caged (open circles) POCIS. Lines represent the prediction from linear regression for uncaged (solid line) and caged (dashed line) POCIS. Black = TNT, blue = 2,4-DNT, green = 2.6-DNT, and red = RDX.

Table C- 2. Regression equations (and r^2) for each of four MC for both uncaged and caged POCIS.

MC	POCIS protection	
	Uncaged	Caged
TNT	0.081fr + 0.014 (0.93)	0.018fr - 0.05 (0.89)
2,4-DNT	0.003fr + 0.052 (0.82)	0.004fr + 0.08 (0.98)
2,6-DNT	0.003fr + 0.065 (0.79)	0.004fr + 0.007 (0.98)
RDX	0.005fr + 0.314 (0.46)	0.008fr + 0.27 (0.53)

C.4 CONCLUSIONS

Because of potential for fluctuating concentrations at contaminated sites, POCIS are considered valuable tools for the environmental exposure assessment of MC in water. The present study demonstrated that the sampling rate of TNT, 2,4- and 2,6-DNT, and RDX increased linearly with flow rate, with the strongest impact on TNT and the weakest impact on RDX. Results indicated that protective canisters mitigate the impact of flow on MC uptake at low flow but not at high flow. Linear regressions describing the change in sampling rate with flow rate should be used for the selection of the most accurate sampling when determining TWA concentrations generated by POCIS deployed at sites contaminated with MC when flow rates are known.

APPENDIX C
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APPENDIX D
COMPOSITION B FLUME STUDY RESULTS

DETECTION OF MUNITIONS CONSTITUENTS USING POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS) UNDER TWO REALISTIC RELEASE SCENARIOS FOR COMPOSITION B

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ABSTRACT

As a result of military training, weapons testing, combat, and historic dumping, underwater military munitions (UWMM) are present in aquatic environments throughout the world. UWMM may corrode, breach, and therefore, may release munitions constituents (MC) into the surrounding aquatic environments. Experiments were conducted in a large flume with a controlled flow set at 15 cm, using realistic exposure scenarios, the first (S1) representing the release of MC from fully exposed Comp B munitions fill and the second (S2) representing the release of MC from Comp B through a small hole, simulating a breached munition object. To evaluate the ability of the polar organic chemical integrative sampler (POCIS) to integrate a slowly increasing MC concentration to accurately estimate time-weighted average (TWA) concentrations, MC in the water was quantified using frequent grab sampling and POCIS, both within and without protective canisters. Overall, the concentrations of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and TNT (2,4,6-trinitrotoluene) in the water increased linearly during the deployment time (10 or 13 days). The uptake of RDX and TNT into uncaged and caged POCIS were not significantly different. For TNT, the POCIS estimated TWA concentrations were 1.2 and 1.4 times higher than those derived from grab samples for S1 and S2, respectively, while for RDX differences were 6% or less, demonstrating that POCIS provide reliable temporal integration of changing environmental concentrations. The release of MC into the flume was also estimated in the context of a numerical model that provides estimations of MC introduced into the surrounding water from an uncovered single breached munition. The predicted and measured TNT release under S2 were within the same order of magnitude, with predicted values exceeding measured values by approximate 3-4 fold over the course of the 13-day experiment.

Key words: Underwater munitions, TNT, RDX, passive sampling, POCIS, flume

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D.1 INTRODUCTION

Underwater sites around the world are known to contain underwater military munitions (UWMM) as a result of military activities or historic dumping events. UWMM have the potential to corrode, breach, and therefore, release munitions constituents (MC), including TNT, RDX, and their major degradation products, into the surrounding aquatic environments (Li et al., 2016; Lewis et al., 2009; Pascoe et al., 2010; Rosen and Lotufo 2010, Wang et al., 2011). Release may also occur from fragments of explosives formulations that become exposed following low-order (incomplete) detonations (LOD).

Release of MC from UWMM from the surrounding environment is expected to be influenced by shell integrity, and concentrations in the surrounding environment are expected to fluctuate over time because of changes in hydrodynamic conditions and the influence of physico-chemical factors, such as sorption to suspended particles or photo-transformation, on the fate of MC at UWMM sites. Standard environmental sampling, such as grab sampling of surface water, that only generate information for the time of sample collection, may inadequately capture substantial changes in concentrations that may occur, thereby not providing an environmentally relevant measure of exposure. For example, if the sample is collected during low environmental concentrations, estimated water concentrations would be biased low. In contrast, integrative passive sampling provides an opportunity to sample MC and obtain time-weighted water concentrations and very low detection limits in water (Belden et al., 2015; Rosen et al., 2016). Commercially available POCIS been proven effective for sampling MC in the water column, including at UWMM sites (Belden et al., 2015; Rosen et al., 2016).

To more fully validate POCIS as an effective tool for characterizing MC contamination in the water column at UWMM sites, more extensive testing using realistic release scenarios that generate fluctuating yet well characterized water concentrations is necessary. Laboratory experiments have demonstrated that POCIS effectively integrate water concentrations of MC under widely fluctuating environmental concentrations and under exposure scenarios simulating MC leaking from a munition through a pinhole (Belden et al., 2015). In the latter study, a Composition B (Comp B) fragment was placed at the bottom of glass aquaria, either fully exposed to represent a LOD exposure scenario or partially encased in a Petri dish perforated on the top with a 0.3 cm hole to represent a small breach exposure scenario in which UWMM are minimally breached or corroded, exposing the explosive fill material within through dissolution and other processes. Those experiments were performed under quasi-static conditions. To further evaluate the ability of POCIS to integrate slowly increasing MC concentrations to accurately estimate time-weighted average concentrations, experiments were conducted in a large flume using two realistic exposure scenarios, one representing the release of MC from fully exposed Comp B munitions fill simulating a LOD and the other representing the release of MC from Comp B through a small hole, simulating a breached munition object. In the current study, the release of MC into the flume water quantified using POCIS was compared to that quantified using frequent grab sampling. The two methods were compared. The release of MC under the scenarios described above was also estimated in the context of a numerical model for MC release from a breached shell with a hole (hereafter Shell Model) (Wang et al., 2011), which provides estimations of MC introduced into the surrounding aquatic environment from the case of an uncovered single breached round.

D.2 EXPERIMENTAL

D.2.1 PASSIVE SAMPLERS AND CHEMICALS

POCIS containing Oasis® hydrophilic–lipophilic balance (HLB) sorbent and stainless steel POCIS holders and protective canisters (cages) (Alvarez et al., 2004) were obtained from Environmental Sampling Technologies (St. Joseph, MO, U.S.A.). Comp B, a common military explosive formulation that consists of 39.5% TNT, 59.5% RDX, and 1% paraffin wax binder by mass, were obtained from the Holston Army Ammunition Plant (Kingsport, TN, USA). Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is an impurity associated with the manufacture of the military-grade RDX used in Comp B, and has been detected in water samples at ~ 10% by mass, of the RDX concentration in related studies (e.g., Rosen and Lotufo, 2010). Because of poor extraction efficiency from water using SPE and high quantitation limits of the GC technique (Belden et al., 2015), this compound was not measured in the present study.

D.2.2 FLUME EVALUATION OF TNT AND RDX RELEASE FROM COMP B

The release of MC from munitions was simulated in experiments conducted in a large flume (Figure D-1). Fragments of Comp B were used as the source of MC to the water column. Two separate experiments simulating the two scenarios (1 and 2) were performed using a surrogate munition (155-mm replica of rubber composition, acquired from Inert Products, LLC, Scranton, PA) that had been cut down the centerline longitudinally, resulting in two ½ munitions with a flat underside that when placed on the floor of the flume would simulate a buried munition with half of its cylindrical projectile surface protruding above the sediment (Figure D-1 and Figure D-supplemental 1). For each ½ surrogate munition, a recessed hole was machined into it for Comp B placement.

Scenario 1 represented the release of MC from fully exposed Comp B munitions fill simulating a LOD. MC release was determined for fully exposed Comp B, without dependence on a breach hole. The dissolution rates for TNT and RDX from a Comp B source matrix into water empirically determined by Lynch et al. (2002) were used. For Scenario 1, the 2-cm hole was machined to a depth of 0.5 cm from the upper cylindrical side of the ½ munition to provide a shallow recessed volume in which Comp B could be placed and fully exposed to the water column and flow velocity in the flume, thus representing a LOD (Figure D-1).

Scenario 2 represented the release of MC from Comp B from a breached munitions for which a small hole simulated the breach hole through which Comp B could be released to the water column as a function of the parameters described by the MC release function (not computer code) developed and validated numerically and empirically by Wang et al. (2013; SERDP ER-1453), hereafter referred to as the Shell Model. The MC release is dependent upon breach hole size, cavity radius, flow velocity in the flume, mass of Comp B in the cavity, and dissolution rate of MC) (Figure D-supplemental 3). The Shell Model is not computer code, but provides a means whereby the release function can be calculated deterministically for scenarios in which these parameters are known (Wang et al., 2011; Wang et al., 2013). For Scenario 2, a 2-cm hole was machined from the flat side of the ½ munition to provide a recessed volume for Comp B, and then a small 1-cm diameter hole was drilled from the bottom of this 2-cm hole completely through the outer cylindrical surface of the ½ munition (Figure D-1). The Shell Model was used to provide an estimation of the mass of TNT and RDX released into the flume water from the surrogate munition under a prescribed flow velocity.

A known amount of Comp B fragments served as the source of MC to the water column. For the Scenario 1 experiment, 13 g of Comp B fragments were fully exposed inside of a shallow cavity on

the upper side of a surrogate shell designed to simulate a partially buried munition (Figure D-1). For Scenario 2 experiment, 8 g of Comp B fragments were placed inside a cylindrical chamber and partially exposed to the overlying water through a 1-cm circular opening to simulate a small breach hole on a surrogate shell designed to simulate a partially buried munition (Figure D-1) for detection of MC in the flume volume.

For both the Scenario 1 and Scenario 2 experiments, POCIS were placed in triplicate at six locations on one side of the flume (Figure D-2 and Figure D-supplemental 2). Four POCIS were located downstream from the Comp B source point (surrogate munition), and two upstream from it (Figure D-2). All samplers were oriented parallel to flow. In addition, three protective metal canisters (cages), with three POCIS per cage, were placed on the side of the flume opposite to the source point (surrogate munition containing Comp B fragments). The target flow velocity was 15 cm/s and the temperature was 25 °C. After all samplers were in place, the flume was filled with approximately 61,000 L of dechlorinated and filtered tap water. Once the target temperature and flow velocity were achieved, the surrogate munition containing Comp B fragments was placed at the designated location (Figure D-2) oriented with nose pointed upstream into the flow direction (Figure D-1c). Flume water (1 L) was collected in duplicate after 0.3, 1.0, 2.3, 3.8, 5.8, 6.9, 8.2, 9.2, and 9.8 d after deployment of the source for the Scenario 1 experiment, and after 3, 5, 7, 9, and 13 days for the Scenario 2 experiment. POCIS were removed from the partially drained flume at termination of the exposure period and stored on dry ice or frozen (-30 °C) until analysis. Exposure duration was approximately 10 and 13 day for the Scenario 1 and 2 experiments, respectively, after deployment to Comp B under constant flow. Following drainage of the flume, Comp B fragments were removed from the surrogate munition, rinsed and placed into a petri dish, allowed to dry at room temperature for approximately one hour, and weighed to the nearest 0.001 g for the calculation of the mass lost to the flume water.

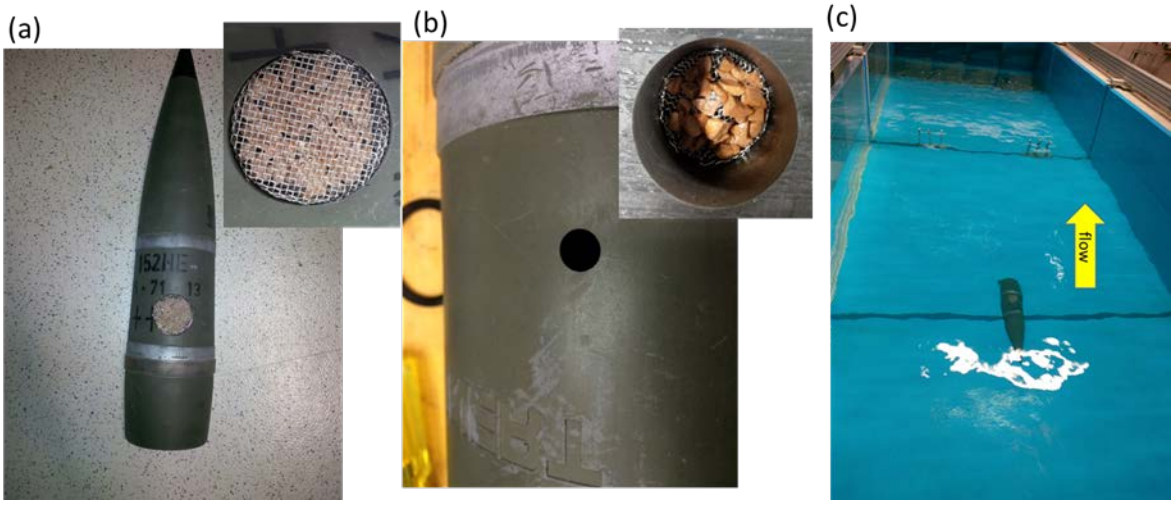

Figure D-1. Half munition surrogate produced from intact full surrogate 155-mm replica loaded with Com B fragments as used in (a) Scenario 1 and (b) Scenario 2 (right) experiments; (c) partial view of the flume showing the surrogate munition containing Comp B fragments as used in Scenario 1 experiment; the yellow arrow indicates the direction of flow.

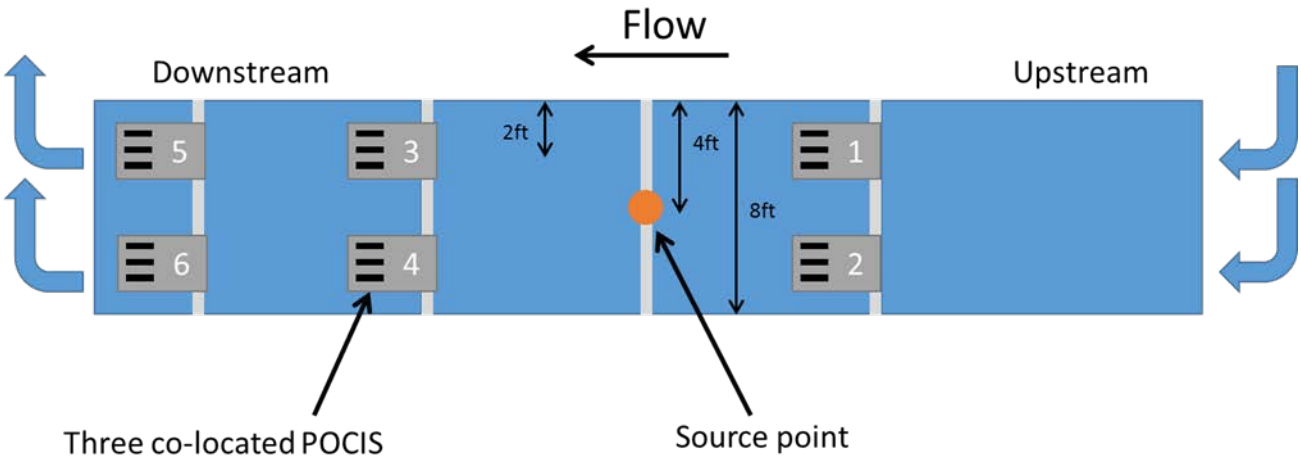

Figure D-2. Schematic showing the locations of the placement of the source point (surrogate munition containing Comp B fragments) and groups of three POCIS mounted on custom-made bases. POCIS placed inside protective canisters were deployed in triplicate canisters in the opposite side of the flume.

D.2.3 RELEASE SCENARIOS

Scenario 1 represented the release of MC from fully exposed Comp B munitions fill simulating a LOD. MC release was determined for fully exposed Comp B, without dependence on a breach hole. The dissolution rates for TNT and RDX from a Comp B source matrix into saltwater empirically determined by Lynch et al. (2002) were used.

Scenario 2 represented the release of MC from Comp B through a small hole, simulating a breached munition. The Shell Model (Wang et al., 2011) was used to provide an estimation of the mass of TNT and RDX that would be released from a small hole under a prescribed flume flow velocity to simulate a breached shell releasing MC into the water column.

D.2.4 EXTRACTION OF WATER AND POCIS AND ANALYSIS BY GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

POCIS and in water samples were analyzed for RDX, TNT, and for the TNT degradation products 2- and 4-aminodinitrotoluenes (2- and 4-ADNT). Water samples (1 L) were extracted by solid-phase extraction (SPE) on Oasis® HLB solid phase extraction (SPE) cartridges (6 ml/500 mg; Waters Corporation, Milford, NH), eluted with ethyl acetate, and brought to a final volume of 0.5 ml using procedures optimized by Belden et al. (2015).

POCIS were disassembled and the sorbent was rinsed into empty SPE tubes. Sorbent from triplicate from each of the eight locations and from each of the three canisters were composited to maximize detection. MCs were eluted with ethyl acetate and brought to a final volume of 0.5 ml. Extracts were analyzed using an Agilent® 6850 GC coupled with a 5975C mass selective detector (MSD) using negative chemical ionization using 3 ion select ion monitoring for each analyte. Internal calibration was performed using ^{13}C-TNT (Belden et al., 2015). The quantitation limits (QL) for RDX and TNT in grab samples were 7.6 and 6.9 ng/L, respectively, and their method detection limits (MDL) were 2.5 and 2.3 ng/L, respectively. For POCIS-derived water concentrations, the QL for RDX and TNT in grab samples were 24 and 25 ng/L, respectively, and their MDL were 18 and 8.4 ng/L, respectively.

D.2.5 CALCULATION OF TIME-AVERAGED CONCENTRATION AND OTHER STATISTICS

The POCIS-derived TWA water concentration was calculated using Equation (1) (Alvarez et al., 2004):

$$C_W = \frac{N}{R_S t} \quad (1)$$

where, C_w is the TWA water concentration (ng/L), N is the mass of amount of the chemical accumulated by the sampler (ng), R_s is the sampling rate (L/day), and t is the exposure time (days). The sampling rate (R_s) derived for TNT and RDX for uncaged POCIS derived from a flume calibration experiment conducted using a flow rate of 15 cm/s (Lotufo et al., 2017) were used to derive C_w.

The effect of protective canister on MC uptake was evaluated for each scenario using t-tests. Each analyte was analyzed independently. Unless otherwise noted, data are expressed as means ± standard deviations. All statistical calculations were performed using Sigma Stat (v.3.5, SYSTAT Software Inc, San Jose, CA) and significance was determined at $\alpha = 0.05$.

D.2.6 PREDICTION OF MC RELEASE USING SHELL MODEL

The Shell Model Equation 1 describes the release function for a breach in a munition casing can be determined by the following five key parameters: (1) the breach hole size (radius of the hole), (2) the radius of the cavity formed due to loss of mass released from inside the shell, (3) the chemical property (dissolution rate) from solid to aqueous phases of the MC inside the shell casing), (4) the outside ambient current to which the casing hole is exposed, and (5) mass of MC remaining inside. For Scenario 1 (LOD), only parameters 3 (dissolution), 4 (ambient current), and 5 (mass remaining), need to be considered as an extreme case where a breach is infinite in size. F is the mass release rate function, which, as depicted in Equation 2, is a closed-form solution with the five variables, including hydrodynamic diffusivity coefficient (*D*), current (*U*), hole size (*b*), cavity radius (*R*) and dissolution speed of MC from solid to aqueous phase (m). The model parameter a, was defined as a geometry factor (Equation 8-1) in Wang et al., 2011) and is typically set to 1:

$$F = \alpha U C(b) \pi b^2 = \frac{2\pi D C_s}{\frac{2D}{\alpha U b^2} + \frac{D}{\mu R^2} + \frac{1}{b} - \frac{1}{R}}. \quad (2)$$

D.3 RESULTS AND DISCUSSION

D.3.1 MC CONCENTRATIONS IN FLUME WATER OVER TIME

The concentrations of RDX, TNT, and 2- and 4-ADNT resulting from dissolution into the flume water over time are shown in Figure D-1. For Scenario 1, the concentration of MC in flume water was within detectable range starting at 7 hours following deployment of the source. Between 2.3 days and the termination of the experiment, the concentration of RDX and TNT in the water increased linearly with time (Figure D-3). The maximum average concentration of TNT and RDX, 12.5 and 17.8 µg/L, respectively, was measured at 6.9 days. Between 6.9 days and the last sampling point at 9.8 days, the concentration of MC in the water remained relatively constant (Figure D-3). A similar linear increase followed by a plateau was observed when Comp B fragments (0.4 g) were placed on a sand substrate in 18 L of water in glass aquaria under static conditions (Rosen and Lotufo 2010). The ratio of explosive compound mass in the fragments and water volume in the flume would allow a maximum dissolved concentration of approximately 126 µg/L for RDX and 84 µg/L for TNT. However, maximum RDX and TNT concentrations in the flume water were lower than these highest attainable levels, consistent with the observation of low loss of Comp B mass at experiment termination (see below). The concentrations of 2- and 4-ADNT were below the method detection limit in all grab samples.

For Scenario 2, the concentration of TNT and RDX increased linearly from the first sampling time (day 3) through the last (day 13) (Figure D-3). The maximum average concentration of TNT and RDX, 1.27 and 1.40 µg/L, respectively, was measured at day 13. The concentrations of 2- and 4-ADNT were substantially lower than those for TNT, contributing to the sum concentration of TNT and ADNTs by ≤ 6%. Linear regressions describing the increase in concentration of TNT and RDX over time are presented in Table D-1.

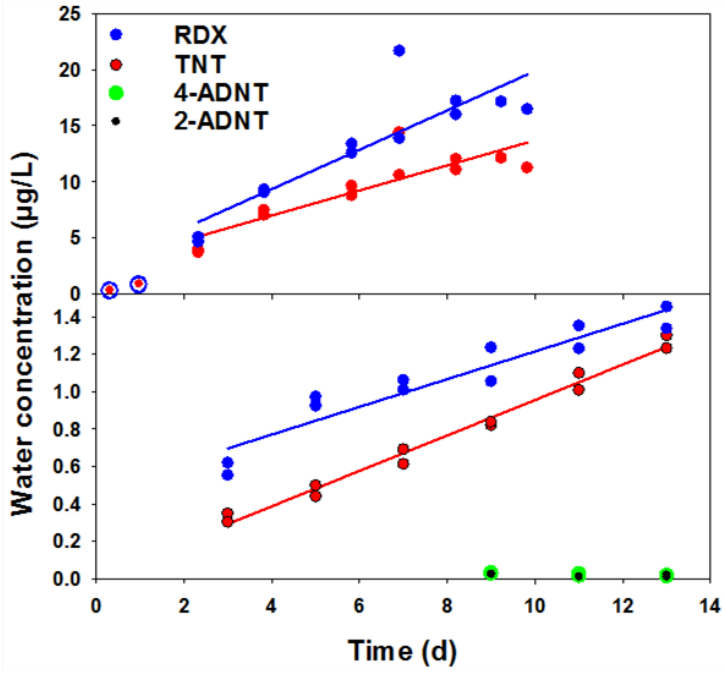

Figure D-3. Individual replicate concentration of RDX (blue) and TNT (red) in flume water (collected as grab samples) over time for the Scenario 1 (top) and Scenario 2 (bottom) experiments. Lines represent the prediction from linear regression.

Table D-1. Regression equations (and r^2) for predicting TNT and RDX concentration (C, µg/L) in the flume water over time for Scenario 1 and Scenario 2 experiments.

MC	Scenario 1	Scenario 2
RDX	C = 1.8 * time (days) + 2.3 (r^2 = 0.76)	C = 0.074 * time (days) + 0.47 (r^2 = 0.90)
TNT	C = 1.2 * time (days) + 2.5 (r^2 = 0.77)	C = 0.094 * time (days) + 0.008 (r^2 = 0.99)

D.3.2 INFLUENCE OF POSITION AND PROTECTIVE CANISTER

For the Scenario 1 experiment, the uptake of RDX and TNT into POCIS was similar across locations in the flume, differing by less than 15% among each other, except for position 4, for which uptake for RDX and TNT were 0.75 and 0.61 that for position 1, respectively (Figure D-5). Position 4 POCIS were situated downstream from the source, which could explain their lower rate of uptake. However, position 3 POCIS, situated on the immediate opposite side of the flume as position 4 POCIS (Figure D-2), had similar uptake as position 1 POCIS. For Scenario 2, differences in uptake between positions were less than 30% for RDX, but higher differences were observed for TNT, notably between positions 1 and 2 and positions 5 and 6, with higher uptake in positions 2 and 6 POCIS (Figure D-4), which were situated at left side of the flume relative to flow direction (Figure D-2).

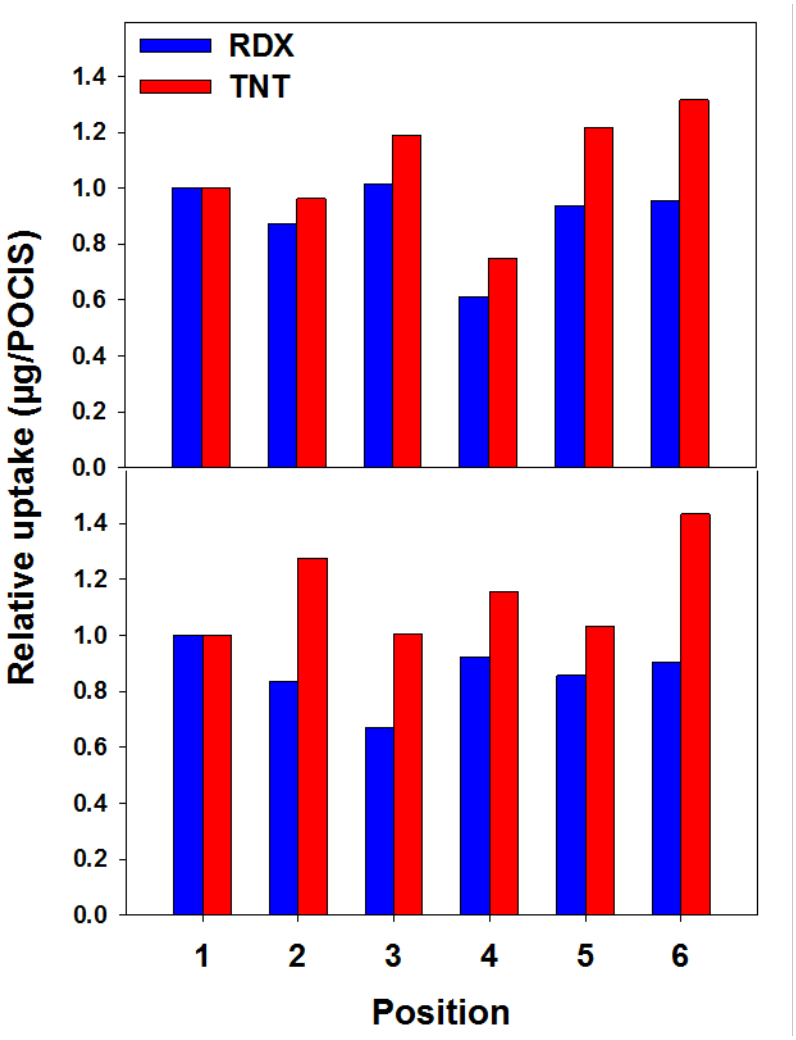

Figure D-4. Comparison of the uptake of RDX (blue) and TNT (red) by POCIS placed at different locations in the flume for the Scenario 1 (top) and Scenario 2 (bottom) experiments. All POCIS were oriented parallel to flow. To simplify comparisons, mass of MC per POCIS for location 1 was arbitrarily assigned the value of 1. Error bars represents standard 1 deviation based upon variability across experiments.

When considering POCIS from positions 1 through 6 as replicates for the uncaged treatment, and POCIS in each of three cages as replicates for the caged treatment, uptake of RDX and TNT into uncaged POCIS and caged POCIS were not significantly different for both Scenarios 1 and 2 ($p > 0.2$) (Figure D-5). This contrasts with the significant decrease in RDX and TNT uptake observed for caged POCIS at 15 cm/s in the spiked MC flume experiment (Lotufo et al., 2017).

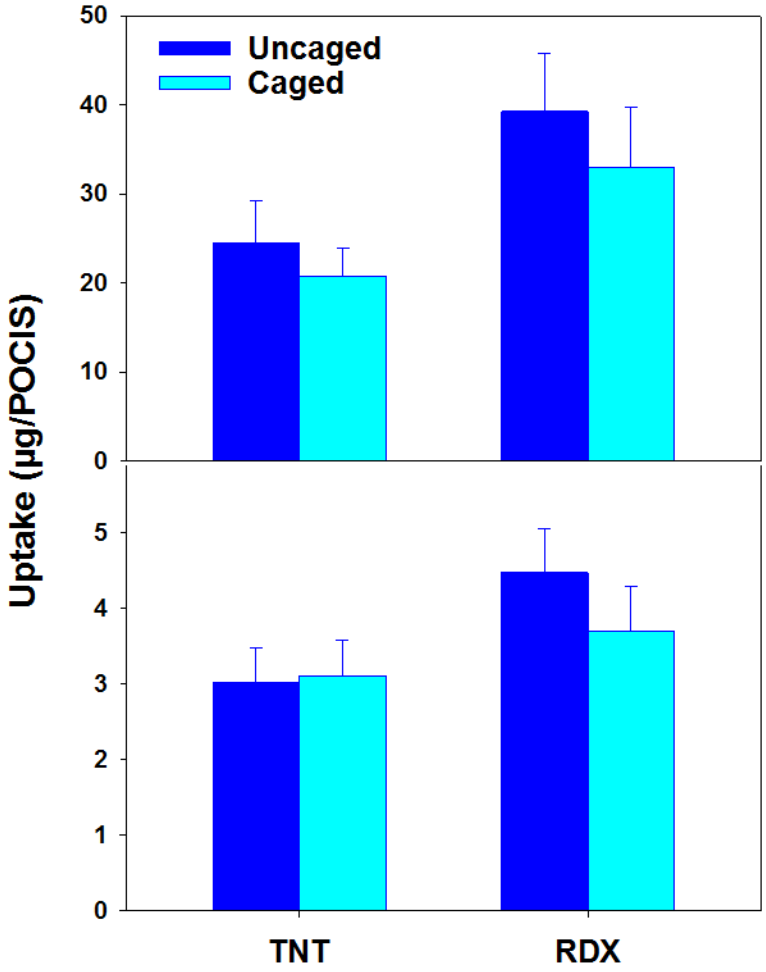

Figure D-5. Comparison of MC uptake in uncaged and caged POCIS for exposure Scenarios 1 (top) and 2 (bottom). Error bars represents 1 standard deviation.

D.3.3 COMPARISON OF GRAB SAMPLING AND POCIS FOR DETERMINING TIME-WEIGHTED AVERAGE CONCENTRATIONS

For grab samples, time-weighted average (TWA) concentrations of RDX and TNT in the flume water were calculated using linear regressions presented in Figure D-4 and Table D-1 as the area under the curve divided by the experiment duration. For Scenario 2, RDX and TNT concentrations between deployment of the source and day 3 were considered zero. For POCIS, TWA concentrations were determined using Equation 1. For TNT, the POCIS estimated TWA concentrations 1.19 and 1.44 time higher than those derived from grab samples for Scenario 1 and 2, respectively (Figure D-7). For RDX, POCIS estimated TWA concentrations were 6% or less higher than those derived from grab samples for Scenario 1 and 2, respectively (Figure D-7). The overall good agreement in estimating water concentration from POCIS and with measured concentrations in water samples was also previously reported from experiments where Comp B was deployed as an open source or encased with only a 0.125-inch hole allowing diffusion (Belden et al., 2015), further confirming the expected accuracy of using POCIS for determining TWA concentrations of MC released to the surrounding water from UWMM. Results from the present study corroborate those from previous

investigations (Terzopoulou and Voutsa 2016; Poulier et al., 2015; Coes et al., 2014) that demonstrated that POCIS provide reliable temporal integration of changing environmental concentrations that would require frequent grab sampling events potentially requiring large volumes of water to obtain comparable temporal integration. In addition, POCIS and POCIS-style samplers sequester residues from episodic events that may not always be detected with grab sampling (Morrison and Belden 2016; Bueno et al., 2016).

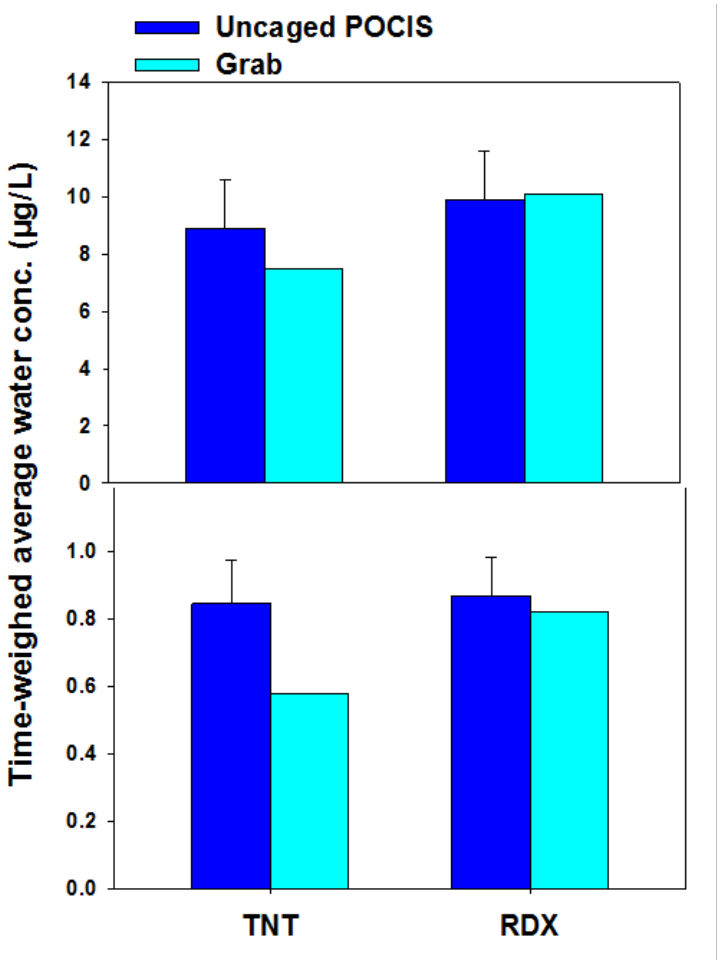

Figure D-6. Comparison of time-weighted average (TWA) concentrations of RDX and TNT in the flume water calculated using Scenarios 1 (top) and 2 (bottom). Error bars represents 1 standard deviation. For grab samples, TWA concentrations were calculated as the area under the curve divided by the experiment duration using linear regressions in Table D-1, hence no error bars.

D.3.4 MC RELEASE

The mass of RDX and time in the flume water at any given time estimated using measured concentration in grab water is presented in Figure D-7. For Scenario 1, a linear increase in mass occurred for RDX and TNT between days 3 and 8, with the mass remaining relatively constant between days 8 and 10 (experiment termination). For Scenario 2, a linear increase in mass occurred for RDX and TNT between days 3 and 13 (experiment termination). The mass of RDX and TNT and

their combined mass in the flume water was calculated using average concentrations measured at day 8 for Scenario 1 and at day 13 for Scenario 2 (Table D-2). The mass of RDX and TNT corresponded to 59 and 41% of the total mass in the water, respectively, for Scenario 1, and 52 and 48% for Scenario 2. The fraction of the total mass in the flume water attributed to RDX corresponded to the fraction of RDX in Comp B for Scenario 1, but was lower than the mass fraction of RDX in Comp B for Scenario 2. Higher fraction of TNT in the flume water was expected considering that the reported dissolution rates of TNT from Comp B was fivefold higher than that of RDX (Lynch, Brannon, and Delfino, 2002). RDX and TNT in Comp B do not dissolve independently, as RDX, which independently dissolves at a relatively much lower rate than TNT, controls the dissolution of the fragment as a whole by limiting the exposed area of TNT (Lever et al., 2005).

The sum mass of RDX and TNT released to the water column from Comp B was also estimated based on the difference in Comp B mass between deployment and recovery (Table D-2). The sum mass of RDX and TNT in the flume water estimated using measured concentration was 80% of the mass estimated from Comp B mass loss, suggesting that losses following dissolution were small. Based on actual mass loss, the relative mass of Comp B released to the flume water during the deployment period was much higher for Scenario 1 (16.5%) than for Scenario 2 (2.0%). The percent loss of Comp B mass during aquaria experiments (Rosen and Lotufo, 2010) where fragments were exposed to water were similar to that observed for Scenario 1. Similarly, the loss reported by Rosen and Lotufo (2010) for buried fragments was similar to that observed for Scenario 2, with sediment and hole size reducing exposure to the overlying water, respectively.

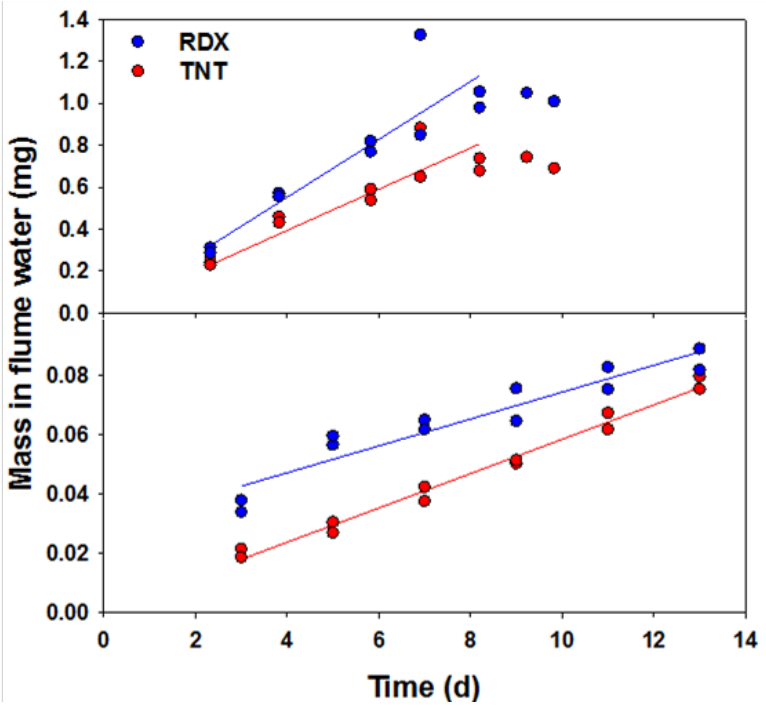

Figure D-7. Mass of RDX (blue) and TNT (red) in flume water over time for the Scenario 1 (top) and Scenario 2 (bottom) experiments estimated using individual replicate concentrations in grab samples. Lines represent the prediction from linear regression.

Table D-2. Estimated mass of RDX and TNT (and their sum) released to the flume water during Scenario 1 and Scenario 2 experiments. Estimates were based on measured concentration in the water or on actual mass loss of Comp B.

Estimated mass released (mg)					
Scenario 1			Scenario 2		
RDX	TNT	Total	RDX	TNT	Total
Based on concentration in the water					
1016	708	1724	85	77	163
Based on Comp B mass loss					
NA	NA	2150	NA	NA	160

D.3.5 SHELL MODEL PREDICTION OF MC CONCENTRATION IN THE WATER

Scenario 1 represents a low order detonation or situation in which munition/MC fill is fully exposed to water. For this scenario, the MC release is equivalent to the munition breach hole being infinite in size, and the Shell Model MC release function is thus equal to the dissolution rate, which was described above.

For Scenario 2, the Shell Model MC release function (Equation 2) was used to ascertain what combination of breach hole size (radius) and internal cavity radius (simulating already dissolved MC) would provide a measurable concentration of TNT in the fixed flume volume, with remaining functional parameters dictated by the test conditions in the flume during MC release. All results for Scenario 2 are based on known values for functional parameters, thus the Shell Model release function was used as a spreadsheet model in a deterministic manner, vice probabilistically using distributions for functional parameters. The results of TNT release calculations are shown below in Table D-3 for various breach sizes (Scenarios 2a-g), showing the behavior as a function of increasing the breach size from sub-µm to the size of the cavity.

Table D-3. Shell Model TNT release function results for various breach sizes for the surrogate munition shown in Figure D-2 for Scenario 2 flume conditions.

	Diffusivity	Solubility	Ambient current	Hole radius	Cavity radius	Dissolution Speed	Release Rate
	D	**Cs**	**U**	**b**	**R**	**mu**	**F**
Scenario 2	m^2/s	mg/L	m/s	m	m	m/s	mg/s
a	6.54E-08	88.5	0.15	0.0000001	0.01	0.0000226	3.7413E-10
b	6.54E-08	88.5	0.15	0.000001	0.01	0.0000226	1.94267E-08
c	6.54E-08	88.5	0.15	0.00001	0.01	0.0000226	3.34705E-07
d	6.54E-08	88.5	0.15	0.0001	0.01	0.0000226	3.63068E-06
e	6.54E-08	88.5	0.15	0.001	0.01	0.0000226	3.91105E-05
f	6.54E-08	88.5	0.15	0.005	0.01	0.0000226	0.000281961
g	6.54E-08	88.5	0.15	0.01	0.01	0.0000226	0.001256284

Subsequent calculations are shown in Table D-4 for estimating the daily MC increase over the course of the Scenario 2 flume experiment using the experimental breach/cavity combination (Scenario 2f, orange) described in section 2.2 above. The daily concentration increase was used to estimate the expected concentration throughout the course of the flume experiment, at approximate concentrations of TNT that were reasonably high enough to detect analytically, thus providing a degree of confidence that the experimental breach hole size was sufficiently large for observable release into the flume volume.

Table D-4. Calculations of daily TNT increase in the flume for the surrogate munition described in Table D-3 for Scenario 2 flume conditions.

	Daily increase in flume			
Scenario 2	mg	mg/L	g/L	ug/L
e	3.37915088	5.5237E-05	5.52365E-08	0.05523655
f	24.3614562	0.00039822	3.98219E-07	0.39821917
g	108.542961	0.00177427	1.77427E-06	1.77427359

Finally, a comparison of predicted TNT concentration by the Shell Model release function to the measured total TNT compounds (TNT + 2-ADNT + 4-ADNT) concentration in the flume for Scenario 2f is shown in Figure D-8. Not only was the predicted TNT release within the same order of magnitude, but also showed good agreement, with only an approximate threefold to fourfold difference observed over the course of the 13-day experiment. It is clear that there are other factors, perhaps related to the surface area of the Comp B source used in the experiment, contributing to the experimental release that the model does not capture adequately, but fortunately the predicted values are slightly over-predicted, i.e., conservative compared to experimental.

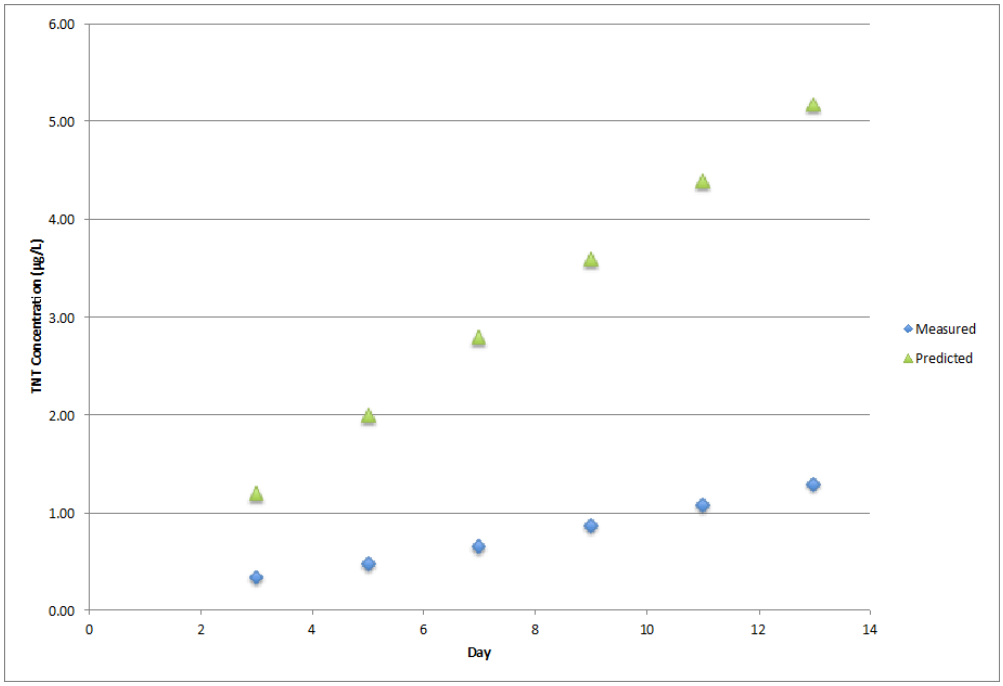

Figure D-8. Comparison of measured TNT concentration vs. predicted TNT concentration using the Shell Model release function under flume conditions for Scenario 2f, which is a three to four time difference.

SUPPLEMENTAL FIGURES

Figure D-supplemental 1. One-half of munition surrogate produced from intact 155-mm replica.

(a) (b) (c)

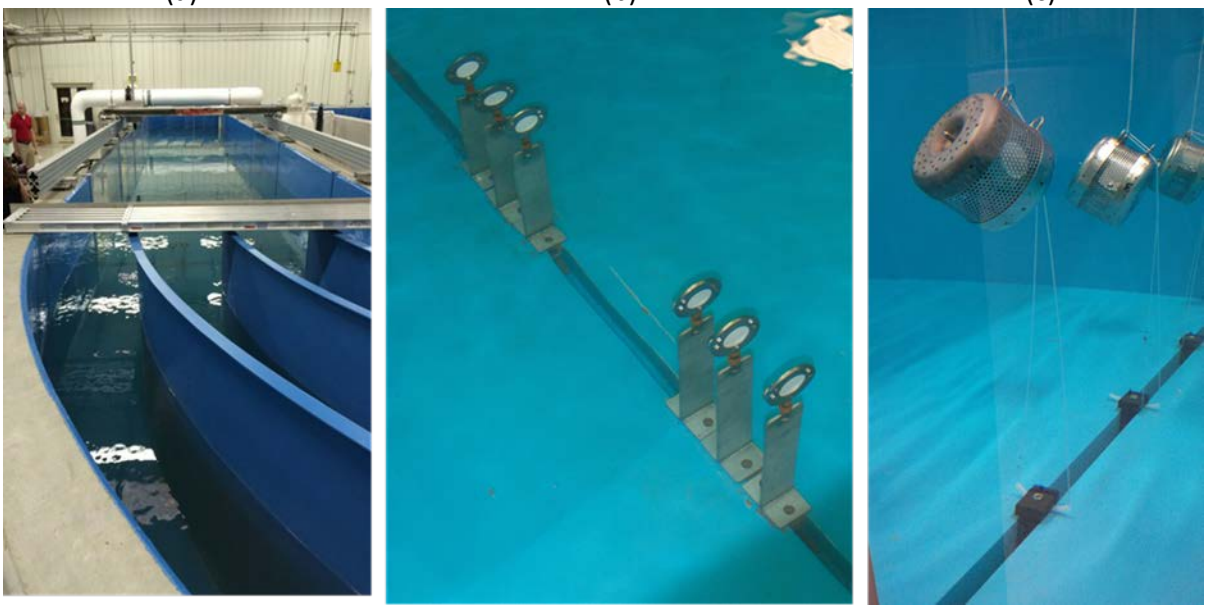

Figure D-supplemental 2. From left to right: (a) partial view of 113,000-L flume, (b) POCIS at one location in the flume, (c) POCIS deployed inside protective canisters.

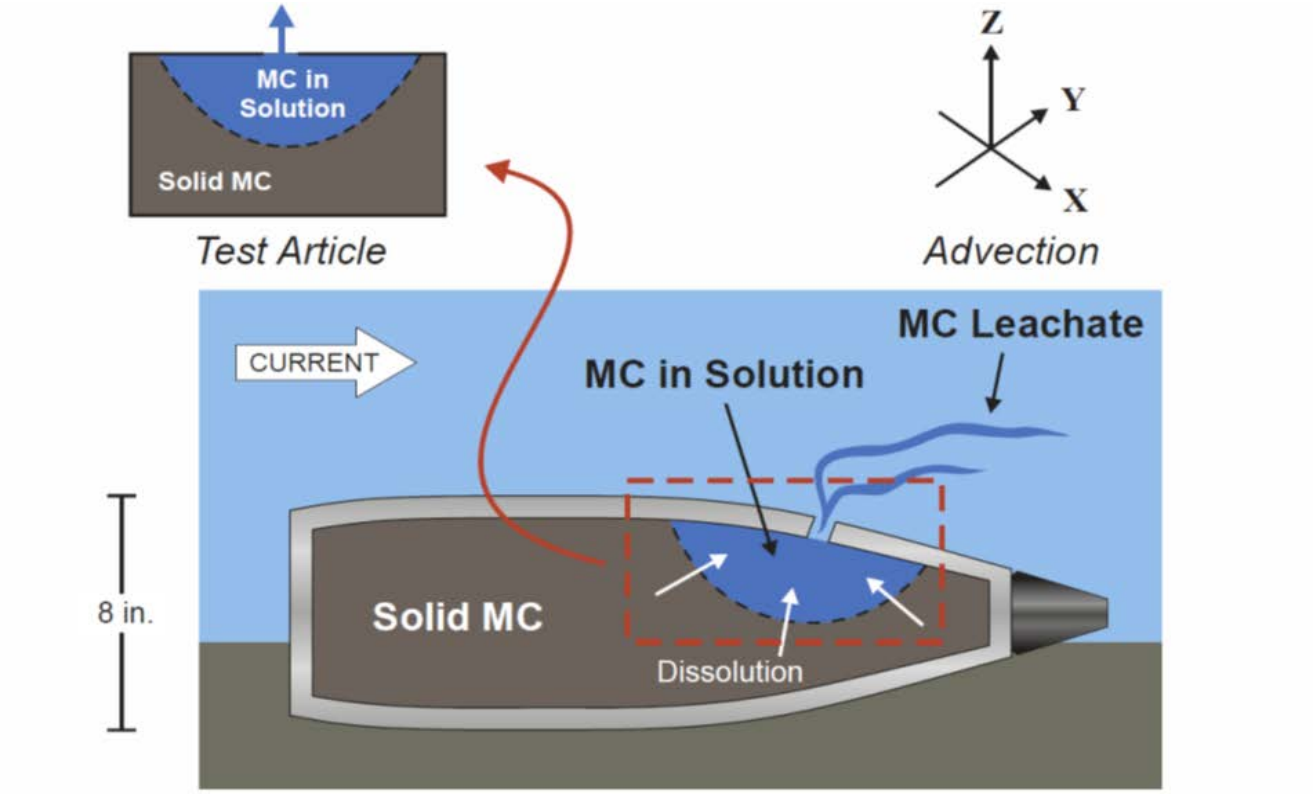

Figure D-supplemental 3. Conceptual model for MC release from a breached shell with a hole (from Wang et al., 2013).

APPENDIX D
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APPENDIX E
ADDITIONAL ANALYTICAL METHOD AND QUALITY CONTROL DETAIL

E.1.1 ANALYSIS OF MUNITIONS CONSTITUENTS FROM POCIS, WATER, TISSUE, AND SEDIMENTS

E.1.1.1 Solvent Elution of POCIS

Following deployment and freezing upon receipt at the analytical laboratory, POCIS assemblies were thawed, disassembled, and HLB resin carefully rinsed into an empty SPE cartridge containing a filtration frit using water. Vacuum was applied to drain all water from the cartridge using a vacuum manifold. A glass test tube was then placed under each cartridge in the vacuum manifold and 15-ml of ethyl acetate was slowly eluted through the HLB resin into the test tube carrying the analytes. The resulting extract was evaporated to 0.5 ml under a gentle stream of nitrogen gas at 30 °C. Final extracts were maintained at -30 °C until analysis. To test for extraction efficiency, across the course of the studies 12 replicate HLB samples were spiked with 1000 ng of each analyte. Average recoveries for each analyte were 92–120% and RSDs ranged from 4–12%. Laboratory blanks, which consist of only reagents, and trip blanks consisting of POCIS that were not deployed but were handled in the field, were also analyzed (n = 10) and no analytes were above quantitation limits.

E.1.1.2 SPE Extraction of water

SPE cartridges (Oasis® HLB cartridges 6 ml/500 mg; Waters Corporation, Milford, NH, USA.) were conditioned by passing 2-ml ethyl acetate, followed by 2-ml methanol, and 10-ml reagent grade water. Collected grab water samples, 1000 ml, were loaded onto a cartridge and passed at a rate of 10–15 ml/min. After the entire sample had passed through the cartridge, air was allowed to pass through for 10 min to dry the cartridge. Cartridges were immediately frozen until shipment and until further analysis could occur. Next, thawed cartridges were centrifuged to remove remaining water, and analytes eluted from the SPE using 10-ml ethyl acetate. The solvent extract was evaporated to 0.5 ml under a gentle stream of nitrogen at 30 °C. Final extracts were frozen until analysis. Several accuracy and precision studies conducted with a total of 16 spiked water samples were used to measure mean extraction efficiency ± standard deviation. Average recovery for analytes ranged from 79–101 with RSD ranging from 4.4–20%. Laboratory blanks and trip blanks were also analyzed (n = 10) and no analytes were detected above quantitation limits.

E.1.1.3 Sediment Extraction

Sediment samples (5 g) from Vieques were extracted three times with 20 ml of acetonitrile using robust vortexing for 2 min and 5 min in a sonicating bath. The combined extract was reduced to a final volume of 1 ml for analysis by GC/MS. Average recoveries for spiked sand for each analyte were 73–87% and RSDs ranged from 1.8–4% (n = 4). Laboratory blanks, which consist of only reagents were also analyzed (n = 2) and no analytes were above quantitation limits.

E.1.1.4 Tissue Extraction

Tissues from the Gulf Breeze positive control field study were extracted using QuEChERS as described by Anastassiades (2003) for pesticides, and optimized for TNT, ADNT, and RDX in Dr. Belden's laboratory as a complementary effort conducted in parallel with the NESDI work (Project #465). The QuEChERS technique involves extraction by acetonitrile followed by cleanup to remove lipids. The initial extraction used was identical to EPA 8330. Sample cleanup was conducted using QuEChERS dispersive kits (Step 2, Aginlent Technologies). Average recoveries for spiked tissue for each analyte were 70–100% and RSDs ranged from 5–12% (n = 4). Laboratory blanks, which consisted of clean oyster tissue were also analyzed (n = 2) and no analytes were above quantitation limits.

E.1.1.5 Analysis by GC-MS

Extracts were analyzed by gas chromatography coupled with mass spectrometry (GC/MS) using GC methods described and optimized by Zhang et al. (2007) and EPA Method 8095 (USEPA, 2007). All extracts were analyzed using an Agilent® 6850 GC coupled with a 5975C MSD detector using negative chemical electron ionization (NCI). The GC inlet was 190 °C with ultra-inert liners (Agilent, Palo Alto, CA), injection volume was 2 µl, and the column was a HP-5MS, 15 m long, 0.25 mm diameter, and 0.25 µm film thickness using a carrier of 1.2 ml/minute helium. The MS was set to have a 150 °C MS quad and a 230 °C MS source. Internal calibration was performed using ^{13}C-labelled TNT as the internal standard.

Calibration curves included five calibration levels and were based on select ion monitoring for each analyte using 3-ions. Instrument quantitation limits were set at 3x the method detection limit calculated based on variability found in seven replicate low level spikes using SPE extracts as background (MDL=student $T_{(n-1,\ 0.99)}$ X SD). Due to sample enrichment, quantitation limits are much lower for SPE and POCIS samples and lower for oyster and sediment samples.

Calibration of the GC/MS was performed prior to each run and checked every 10 samples. Precision and accuracy of all laboratory analytical data were monitored throughout the analytical process. Instrument precision and accuracy was assured by conducting initial calibration curves ($r2 > 0.98$), and continuing calibration verification at a frequency of 10%. Continuing calibration did not exceed 20% of expected value prior and post the sample run for data to be valid. Calibration and maintenance of the MS is conducted prior to every analytical run including checking the accuracy of the tune and checking for leaks.

E.1.1.6 Picric Acid by HPLC

Picric acid analysis was conducted by a HPLC-UV analysis (modified EPA 8330b) as described by Thorne and Jenkins (1995). POCIS extracts were diluted 1:1 with mobile phase (60:40 (v/v) aqueous buffer:methanol. The buffer was 0.05 M KH2P04 adjusted to pH 3.5 with acetic acid). Analysis was conducted by UV at 365 nm for picrate.

APPENDIX E
REFERENCES

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APPENDIX F
PERMITS AND SENSITIVE SPECIES CONSIDERATIONS

DEPARTMENT OF THE NAVY
NAVAL ORDNANCE SAFETY AND SECURITY ACTIVITY
FARRAGUT HALL
3817 STRAUSS AVENUE, SUITE 108
INDIAN HEAD, MD 20640-5151

8020
Ser N49/947
24 Jun 15

From: Commanding Officer, Naval Ordnance Safety and Security Activity
To: Commanding Officer, Naval Facilities Engineering Command, Atlantic (EV31DH)

Subj: EXPLOSIVES SAFETY SUBMISSION DETERMINATION REQUEST FOR ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM VALIDATION STUDY FOR MUNITIONS CONSTITUENTS AT THE FORMER VIEQUES NAVAL TRAINING RANGE, VIEQUES, PUERTO RICO

Ref: (a) E-mail NAVFAC LANT (EV31DH) Mr. D. Hood/ NOSSA (N49) Mr. P. Altman of 17 Jun 15 (w/encl)
(b) NOSSAINST 8020.15D
(c) NAVSEA OP 5, Volume 1, Seventh Revision, Change 13

1. As requested by reference (a), the Naval Ordnance Safety and Security Activity (NOSSA) reviewed the subject Explosives Safety Submission (ESS) Determination Request (DR) in accordance with references (b) and (c). Based on the information provided, NOSSA has determined that an ESS is not required to conduct the validation study of passive sampling devices for munitions constituents in the waters surrounding the former Vieques Naval Training Range (VNTR), Vieques, Puerto Rico.

2. As outlined in your request, we understand that the likelihood of encountering Munitions and Explosives of Concern (MEC) and/or Material Potentially Presenting an Explosive Hazard (MPPEH) during the proposed project has been determined to be low and that the following conditions apply:

a. Anomaly avoidance techniques shall be employed by unexploded ordnance qualified personnel during operations to avoid contact with MEC or MPPEH. No intentional physical contact or other intrusive activities with MEC/MPPEH are authorized.

Subj: EXPLOSIVES SAFETY SUBMISSION DETERMINATION REQUEST FOR ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM VALIDATION STUDY FOR MUNITIONS CONSTITUENTS AT THE FORMER VIEQUES NAVAL TRAINING RANGE, VIEQUES, PUERTO RICO

b. The non-intrusive sampling method will involve anchoring sampling units to the sea floor using weights. If a more robust anchoring system is required such as stakes or sand anchors, anomaly avoidance will be used prior to placing items on the seafloor.

c. The sampling units will be removed practicing anomaly avoidance as well.

d. All personnel who are performing operations defined in this ESS DR are considered nonessential personnel with respect to the munitions response operations being conducted at VNTR. Contact the responsible project manager for required minimum separation distances from the munitions response operations being conducted.

3. If underwater MEC or MPPEH is discovered during the operation, the item will be avoided and its location and description will be recorded and reported to the responsible Explosives Safety Officer and the project manager. An emergency response from the cognizant Explosive Ordnance Disposal detachment will be requested, if appropriate.

4. The NOSSA point of contact for this ESS DR is Mr. Pat Altman, who can be contacted at 301-744-5630.

TAMMY K. SCHIRF
By direction

Copy to:
CNO (N411B; N452)
COMNAVFACENGCOM (ENV3)
COMNAVREG SE Jacksonville (ESO)
NOSSA ESSOLANT (N5L)
NOSSA (N545)

DEPARTMENT OF THE ARMY
JACKSONVILLE DISTRICT CORPS OF ENGINEERS, ANTILLES OFFICE
ANNEX BUILDING, FUNDACIÓN ÁNGEL RAMOS
2ND FLOOR, SUITE 202
FRANKLIN DELANO ROOSEVELT AVENUE #383
SAN JUAN, PUERTO RICO 00917

REPLY TO
ATTENTION OF

September 17, 2015

Regulatory Division
South Permits Branch
Antilles Permits Section
SAJ-2015-02822(NPR-JMS)

Gunther H. Rosen
US Navy/Space and Naval Warfare Systems Center
53475 Strothe Rd.
San Diego, CA 92152

Dear Mr. Rosen:

Reference is made to the application received on September 03, 2015, for a Department of the Army permit for deployment of scientific devices to demonstrate the utility of integrative passive sampling devices such as POCIS, for low-level detection of munitions constituents. The proposed project site is located at Bahia Salina del Sur site in Vieques, PR. The application has been assigned file number SAJ-2015-02822.

Based upon the information provided, the proposed work has been determined to be an activity undertaken entirely by a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site by authority of CERCLA as approved or required by EPA, and is not required to obtain permits under Section 404 of the Clean Water Act or Section 10 of the Rivers and Harbors Act.

This letter does not obviate the requirement to obtain any other Federal, State, or local permits that may be necessary for your project. Should you have any questions, please contact Johann M. Sasso at the letterhead address, by electronic mail at johann.m.sasso@usace.army.mil, or by telephone at 787-729-6905 extension 3053.

Thank you for your cooperation with our permit program. The Corps Jacksonville District Regulatory Division is committed to improving service to our customers. We strive to perform our duty in a friendly and timely manner while working to preserve our environment. We invite you to complete our automated Customer Service Survey at http://corpsmapu.usace.army.mil/cm_apex/f?p=regulatory_survey . Please be aware this Internet

address is case sensitive; and, you will need to enter it exactly as it appears above. Your input is appreciated – favorable or otherwise.

Sincerely,

Sindulfo Castillo
Chief, Antilles Regulatory Section

Copies Furnished:

EPA:
U. S. Environmental Protection Agency Vieques Field Office Vieques Office Park
Carretera # 200, km 0.4 Vieques, P.R. 00765

U.S. Environmental Protection Agency Caribbean Environmental Protection Division
1492 Ponce de Leon Centro Europa Building - Suite 417 San Juan, P.R. 00907-4127

Vessel Strike Avoidance Measures and Reporting for Mariners
NOAA Fisheries Service, Southeast Region

Background
The National Marine Fisheries Service (NMFS) has determined that collisions with vessels can injure or kill protected species (e.g., endangered and threatened species, and marine mammals). The following standard measures should be implemented to reduce the risk associated with vessel strikes or disturbance of these protected species to discountable levels. NMFS should be contacted to identify any additional conservation and recovery issues of concern, and to assist in the development of measures that may be necessary.

Protected Species Identification Training
Vessel crews should use an Atlantic and Gulf of Mexico reference guide that helps identify protected species that might be encountered in U.S. waters of the Atlantic Ocean, including the Caribbean Sea, and Gulf of Mexico. Additional training should be provided regarding information and resources available regarding federal laws and regulations for protected species, ship strike information, critical habitat, migratory routes and seasonal abundance, and recent sightings of protected species.

Vessel Strike Avoidance
In order to avoid causing injury or death to marine mammals and sea turtles the following measures should be taken when consistent with safe navigation:

1. Vessel operators and crews shall maintain a vigilant watch for marine mammals and sea turtles to avoid striking sighted protected species.

2. When whales are sighted, maintain a distance of 100 yards or greater between the whale and the vessel.

3. When sea turtles or small cetaceans are sighted, attempt to maintain a distance of 50 yards or greater between the animal and the vessel whenever possible.

4. When small cetaceans are sighted while a vessel is underway (e.g., bow-riding), attempt to remain parallel to the animal's course. Avoid excessive speed or abrupt changes in direction until the cetacean has left the area.

5. Reduce vessel speed to 10 knots or less when mother/calf pairs, groups, or large assemblages of cetaceans are observed near an underway vessel, when safety permits. A single cetacean at the surface may indicate the presence of submerged animals in the vicinity; therefore, prudent precautionary measures should always be exercised. The vessel shall attempt to route around the animals, maintaining a minimum distance of 100 yards whenever possible.

NMFS Southeast Region Vessel Strike Avoidance Measures and Reporting for Mariners; revised February 2008.

6. Whales may surface in unpredictable locations or approach slowly moving vessels. When an animal is sighted in the vessel's path or in close proximity to a moving vessel and when safety permits, reduce speed and shift the engine to neutral. Do not engage the engines until the animals are clear of the area.

Additional Requirements for the North Atlantic Right Whale

1. If a sighted whale is believed to be a North Atlantic right whale, federal regulation requires a minimum distance of 500 yards be maintained from the animal (50 CFR 224.103 (c)).

2. Vessels entering North Atlantic right whale critical habitat are required to report into the Mandatory Ship Reporting System.

3. Mariners shall check with various communication media for general information regarding avoiding ship strikes and specific information regarding North Atlantic right whale sighting locations. These include NOAA weather radio, U.S. Coast Guard NAVTEX broadcasts, and Notices to Mariners. Commercial mariners calling on United States ports should view the most recent version of the NOAA/USCG produced training CD entitled "A Prudent Mariner's Guide to Right Whale Protection" (contact the NMFS Southeast Region, Protected Resources Division for more information regarding the CD).

4. Injured, dead, or entangled right whales should be immediately reported to the U.S. Coast Guard via VHF Channel 16.

Injured or Dead Protected Species Reporting

Vessel crews shall report sightings of any injured or dead protected species immediately, regardless of whether the injury or death is caused by your vessel.

Report marine mammals to the Southeast U.S. Stranding Hotline: 877-433-8299
Report sea turtles to the NMFS Southeast Regional Office: 727-824-5312

If the injury or death of a marine mammal was caused by a collision with your vessel, responsible parties shall remain available to assist the respective salvage and stranding network as needed. NMFS' Southeast Regional Office shall be immediately notified of the strike by email (takereport.nmfsser@noaa.gov) using the attached vessel strike reporting form.

For additional information, please contact the Protected Resources Division at:

NOAA Fisheries Service
Southeast Regional Office
263 13th Avenue South
St. Petersburg, FL 33701
Tel: (727) 824-5312
Visit us on the web at http://sero.nmfs.noaa.gov

NMFS Southeast Region Vessel Strike Avoidance Measures and Reporting for Mariners; revised February 2008.

Standard Operating Procedures for Protection of Federally Listed Species and Sensitive Habitat

Underwater Site Inspections of Former Anchorage Areas and Offshore Areas in the Vicinity of the Former OB/OD Area

Former Navy Facility
Vieques, Puerto Rico

These Standard Operating Procedures (SOPs) apply to the work activities identified in the *Quality Assurance Project Plan for Underwater Site Inspections of Former Anchorage Areas and Offshore Areas in the Vicinity of the Former OB/OD Area, Former Navy Facility, Vieques, Puerto Rico, June 2012.* All work personnel are required to review and implement these SOPs. These SOPs are required to be posted onboard all work vessels.

Vessel Operations

- All vessels will be operated at no wake/idle speeds at all times while in water depths where the draft of the vessel provides less than 4 feet clearance from the seafloor.
- All vessels will preferentially follow deep water routes whenever possible.
- Vessel operators will review nautical charts and use onboard depth sounders to prevent vessel contact with the seafloor.
- Vessels will be anchored preferentially on sandy bottom whenever possible. If anchoring on sandy bottom is not possible, vessels may be anchored on vegetated bottom that consists of seagrass and/or algae (seaweed). Vessels will not be anchored on hardbottom that contains hard and/or soft coral, regardless of the percentage of coral cover present. The type of bottom present will be confirmed by divers, onboard using a glass-bottom bucket, or by other appropriate means, prior to anchoring.
- If the vessel is anchored on vegetated bottom (seagrass/algae), the anchor will be removed from the seafloor in a manner that minimizes disturbance to the vegetation as follows:
  - by attaching a secondary anchor line to the rear of any plow-type anchor (danforth, union, bruce) and pulling the anchor free from the seafloor before lifting to the surface, or
  - by having a diver remove the anchor from the seafloor manually underwater

Protection of Sea Turtles and Marine Mammals

- All work personnel will be familiar with the identification of federally listed sea turtle and marine mammal species that have the potential to occur in the work areas; ESA policy and associated civil/criminal penalties for violations; and the procedures to be followed to prevent impacts to sea turtles and marine mammals during work activities.
- The following federally listed sea turtle species have the potential to occur in the work areas:

- Loggerhead sea turtle (*Caretta caretta*)
- Green sea turtle (*Chelonia mydas*)
- Leatherback sea turtle (*Dermochelys coriacea*)
- Hawksbill sea turtle (*Eretmochelys imbricata*)

- The following federally listed marine mammal species have the potential to occur in the work areas:

- West Indian manatee (*Trichechus manatus*)
- Humpback whale (*Megaptera novaeangliae*)
- Sperm whale (*Physeter macrocephalus*)
- Sei whale (*Balaenoptera borealis*)
- Blue whale (*Balaenoptera musculus*)
- Finback whale (*Balaenoptera physalus*)

- All personnel onboard work vessels are responsible for observing for the presence of sea turtles and marine mammals. The work areas will be routinely monitored for the presence of sea turtles and marine mammals both underwater and above water.
- If a whale is sighted, maintain a distance of 100 yards or greater between the whale and the vessel whenever possible.
- If a sea turtle or manatee is sighted, maintain a distance of 50 yards or greater between the animal and the vessel whenever possible.
- If a whale is sighted while a vessel is underway (e.g., bow-riding), attempt to remain parallel to the animal's course. Avoid excessive speed or abrupt changes in direction until the whale has left the area.
- Reduce vessel speed to 10 knots or less when mother/calf pairs, groups, or large assemblages of whales are sighted near an underway vessel, when safety permits. A single whale at the surface may indicate the presence of submerged animals in the vicinity. The vessel should attempt to route around the animals, maintaining a minimum distance of 100 yards whenever possible.
- Sea turtles and marine mammals may surface in unpredictable locations or approach slowly moving vessels. When an animal is sighted in the vessel's path or in close proximity to a moving vessel, reduce speed and shift the engine to neutral. Do not engage the engines until the animal is clear of the area.
- Any collision with and/or injury to a sea turtle or marine mammal will be reported immediately to NMFS. Work personnel should report sightings of any injured or dead sea turtle or marine mammal immediately to NMFS, regardless of whether the injury/death is caused by the work personnel.
- Report sea turtles to the NMFS Southeast Regional Office: (727) 824-5312.
- Report marine mammals to the Southeast U.S. Stranding Hotline: (877) 433-8299.
- If the injury or death of a sea turtle or marine mammal is caused by a vessel collision or other work activity, the responsible parties will remain available to assist the respective response personnel as needed.

Diving and Anomaly Removal Operations

- All work personnel will be familiar with the identification of federally listed coral species, hardbottom habitat, and vegetated bottom habitat that have the potential to occur in the work areas; ESA policy and associated civil/criminal penalties for violations; and the procedures to be followed to prevent impacts to listed coral species, hardbottom habitat, and vegetated bottom habitat during work activities.
- The following federally listed coral species have the potential to occur in the work areas:

- Staghorn coral (*Acropora cervicornis*)
- Elkhorn coral (*Acropora palmata*)

- In addition to staghorn and elkhorn coral, there are seven federal candidate coral species that have the potential to occur in the work areas. As standard practice, impacts to any hard or soft coral species should be avoided.
- Divers will limit physical contact with the benthic environment to the minimum extent needed to effectively conduct the work identified in the Quality Assurance Project Plan.

- Underwater metal detector surveys may be conducted over any type of bottom; however, removal of surface anomalies and excavation/removal of subsurface anomalies will occur only on sandy bottom or vegetated bottom (seagrass/algae), not on hardbottom (hard/soft coral).
- Turbidity (sediment suspension) will be minimized to the extent possible during all underwater work activities. Although excessive turbidity is not expected to be generated by the underwater work activities, turbidity will be visually monitored and prudent measures will be taken to minimize turbidity generation.
- Anomalies determined safe to remove will be removed manually by hand and/or using hand-held tools. No underwater detonations will be conducted.
- All removed anomalies will be transported to agency-approved terrestrial detonation/disposal areas.
- Excavations to inspect/remove subsurface anomalies will be limited to a depth of 1 foot below the seafloor.
- The disturbance footprint of the seafloor during subsurface anomaly excavations will be limited to approximately 2 square feet whenever possible.
- All excavations of the seafloor will be backfilled to match the pre-excavation grade to the extent possible.
- Any seagrass that is removed during anomaly excavations will be immediately replanted by hand in the same area. When excavating in seagrass areas, divers will attempt to maintain the integrity of the root/rhizome structure of any seagrass that must be removed so that intact seagrass plugs are removed and replanted to the extent possible.

Dive Safety Plan for
Validation of Passive Sampling Devices for
Monitoring of Munitions Constituents
In Underwater Environments

Former Vieques Naval Training Range
Vieques, Puerto Rico

Prepared by

Virginia Beach, Virginia

Lora Pride/NWO-AAUS Dive Safety Officer (DSO) and Science Dive Lead (SDL)

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION
160 W GOVERNMENT STREET, SUITE 308
PENSACOLA, FLORIDA 32502-5794

RICK SCOTT
GOVERNOR

JENNIFER CARROLL
LT. GOVERNOR

HERSCHEL T. VINYARD JR.
SECRETARY

March 05, 2013

BY ELECTRONIC MAIL: Gunther.Rosen@navy.mil

Space and Naval Warfare Systems Center Pacific (US Navy)
Attn: Gunther Rosen
Code 71760, 53472 Strothe Rd
San Diego, CA 92152

Dear Mr. Rosen:

On February 22, 2013, we received your application File no.: 57-316874-001-EE to perform the following activities:

Conduct a research study utilizing ultra-trace level concentrations of military-relevant munitions constituents (e.g., TNT, RDX) and passive sampler devices for a total exposure time of approximately 2 weeks in Santa Rosa Sound, a Class III Outstanding Florida Waterbody. The activities will be conducted at the USEPA Gulf Ecology Division, One Sabine Island Drive, Gulf Breeze, FL 32561 at Latitude/Longitude 30° 20' 19.19" N/87° 9' 21.40"W.

Your application has been reviewed to determine whether it qualifies for (1) regulatory authorization; and (2) any required authorization to use state-owned (sovereign) submerged lands owned by the state of Florida.

1. Regulatory Review – EXEMPTION VERIFIED

Based on the information submitted, the Department has determined that the research activity is exempt, under section 373.406(6) of the Florida Statutes, from the need to obtain a regulatory permit under part IV of chapter 373 of the Florida Statutes. This determination is made because the activity, in consideration of its type, size, nature, location, use, and operation, is expected to have only minimal or insignificant individual or cumulative adverse impacts on the water resources.

Therefore, the Department grants a de minimis exemption for the proposed activity under section 373.406(6), F.S.

This exemption verification is based on the information you provided the Department and the statutes and rules in effect when the information was submitted. This verification will expire after one year, and will not be valid at any other time if site conditions materially change, the project design is modified, or the statutes or rules governing the exempt activity are amended. However, the activity may still be conducted without further

notification to or verification from the Department after the one-year expiration of this verification, provided: 1) the project design does not change; 2) site conditions do not materially change; and 3) there are no changes to the statutes or rules governing the exempt activity. In the event you need to re-verify the exempt status for the activity after the one-year expiration of this verification, a new application and verification fee will be required. Any substantial modifications to the project design should be submitted to the Department for review, as changes may result in a permit being required.

2. **Authorization to use state-owned (sovereign) submerged lands** – Granted

The Department acts as staff to the Board of Trustees of the Internal Improvement Trust Fund (Board of Trustees) and issues certain authorizations for the use of sovereign submerged lands. The Department has the authority to review activities on sovereign submerged lands under chapters 253 and 258 of the Florida Statutes, and chapters 18-20 and 18-21 of the Florida Administrative Code.

The activity appears to be located on sovereign submerged lands owned by the Board of Trustees. The activity is not exempt from the need to obtain the applicable proprietary authorization. As staff to the Board of Trustees, the Department has reviewed the activity described above, and has determined that the activity qualifies for a consent of use under section 253.77, Florida Statutes, and Rule 18-21.005(1)(c)(16), F.A.C., to construct and use the activity on the specified sovereign submerged lands, as long as the work performed is located within the boundaries as described herein and is consistent with the terms and conditions herein.

General Conditions for State-Owned Submerged Land Authorizations:
(a) Authorizations are valid only for the specified activity or use. Any unauthorized deviation from the specified activity or use and the conditions for undertaking that activity or use shall constitute a violation. Violation of the authorization shall result in suspension or revocation of the grantee's use of the sovereignty submerged land unless cured to the satisfaction of the Board.

(b) Authorizations convey no title to sovereignty submerged land or water column, nor do they constitute recognition or acknowledgment of any other person's title to such land or water.

(c) Authorizations may be modified, suspended or revoked in accordance with their terms or the remedies provided in Sections 253.04 and 258.46, F.S., or Chapter 18-14, F.A.C.

(d) Structures or activities shall be constructed and used to avoid or minimize adverse impacts to sovereignty submerged lands and resources.

(e) Construction, use, or operation of the structure or activity shall not adversely affect any species which is endangered, threatened or of special concern, as listed in Rules 68A-27.003, 68A-27.004, and 68A-27.005, F.A.C.

(f) Structures or activities shall not unreasonably interfere with riparian rights. When a court of competent jurisdiction determines that riparian rights have been unlawfully affected, the structure or activity shall be modified in accordance with the court's decision.

(g) Structures or activities shall not create a navigational hazard.

(h) Structures shall be maintained in a functional condition and shall be repaired or removed if they become dilapidated to such an extent that they are no longer functional. This shall not be construed to prohibit the repair or replacement subject to the provisions of Rule 18-21.005, F.A.C., within one year, of a structure damaged in a discrete event such as a storm, flood, accident, or fire.

(i) Structures or activities shall be constructed, operated, and maintained solely for water dependent purposes, or for non-water dependent activities authorized under paragraph 18-21.004(1)(f), F.A.C., or any other applicable law.

Additional Information
This letter does not relieve you from the responsibility of obtaining other federal, state, or local authorizations that may be required for the activity.

Please retain this letter. The activities may be inspected by authorized state personnel in the future to insure compliance with appropriate statutes and administrative codes. If the activities are not in compliance, you may be subject to penalties under Chapter 373, F.S., and Chapter 18-14, F.A.C.

NOTICE OF RIGHTS
This action is final and effective on the date filed with the Clerk of the Department unless a petition for an administrative hearing is timely filed under Sections 120.569 and 120.57, F.S., before the deadline for filing a petition. On the filing of a timely and sufficient petition, this action will not be final and effective until further order of the Department. Because the administrative hearing process is designed to formulate final agency action, the filing of a petition means that the Department's final action may be different from the position taken by it in this notice.

Petition for Administrative Hearing
A person whose substantial interests are affected by the Department's action may petition for an administrative proceeding (hearing) under Sections 120.569 and 120.57, F.S. Pursuant to Rule 28-106.201, F.A.C., a petition for an administrative hearing must contain the following information:

(a) The name and address of each agency affected and each agency's file or identification number, if known;
(b) The name, address, and telephone number of the petitioner; the name, address, and telephone number of the petitioner's representative, if any, which shall be the address for service purposes during the course of the proceeding; and an explanation of how the petitioner's substantial interests are or will be affected by the agency determination;

(c) A statement of when and how the petitioner received notice of the agency decision;

(d) A statement of all disputed issues of material fact. If there are none, the petition must so indicate;

(e) A concise statement of the ultimate facts alleged, including the specific facts that the petitioner contends warrant reversal or modification of the agency's proposed action;

(f) A statement of the specific rules or statutes that the petitioner contends require reversal or modification of the agency's proposed action, including an explanation of how the alleged facts relate to the specific rules or statutes; and

(g) A statement of the relief sought by the petitioner, stating precisely the action that the petitioner wishes the agency to take with respect to the agency's proposed action.

The petition must be filed (received by the Clerk) in the Office of General Counsel of the Department at 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000. Also, a copy of the petition shall be mailed to the applicant at the address indicated above at the time of filing.

Time Period for Filing a Petition

In accordance with Rule 62-110.106(3), F.A.C., petitions for an administrative hearing by the applicant must be filed within 14 days of receipt of this written notice. Petitions filed by any persons other than the applicant, and other than those entitled to written notice under Section 120.60(3), F.S. must be filed within 14 days of publication of the notice or within 14 days of receipt of the written notice, whichever occurs first. Under Section 120.60(3), F.S., however, any person who has asked the Department for notice of agency action may file a petition within 14 days of receipt of such notice, regardless of the date of publication. The failure to file a petition within the appropriate time period shall constitute a waiver of that person's right to request an administrative determination (hearing) under Sections 120.569 and 120.57, F.S., or to intervene in this proceeding and participate as a party to it. Any subsequent intervention (in a proceeding initiated by another party) will be only at the discretion of the presiding officer upon the filing of a motion in compliance with Rule 28-106.205, F.A.C.

Extension of Time

Under Rule 62-110.106(4), F.A.C., a person whose substantial interests are affected by the Department's action may also request an extension of time to file a petition for an administrative hearing. The Department may, for good cause shown, grant the request for an extension of time. Requests for extension of time must be filed with the Office of General Counsel of the Department at 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000, before the applicable deadline for filing a petition for an administrative hearing. A timely request for extension of time shall toll the running of the time period for filing a petition until the request is acted upon.

Mediation

Mediation is not available in this proceeding.

FLAWAC Review

The applicant, or any party within the meaning of Section 373.114(1)(a) or 373.4275, F.S., may also seek appellate review of this order before the Land and Water Adjudicatory Commission under Section 373.114(1) or 373.4275, F.S. Requests for review before the Land and Water Adjudicatory Commission must be filed with the Secretary of the Commission and served on the Department within 20 days from the date when the order is filed with the Clerk of the Department.

Judicial Review

Any party to this action has the right to seek judicial review pursuant to Section 120.68, F.S., by filing a Notice of Appeal pursuant to Rules 9.110 and 9.190, Florida Rules of Appellate Procedure, with the Clerk of the Department in the Office of General Counsel, 3900 Commonwealth Boulevard, M.S. 35, Tallahassee, Florida 32399-3000; and by filing a copy of the Notice of Appeal accompanied by the applicable filing fees with the appropriate District Court of Appeal. The Notice of Appeal must be filed within 30 days from the date this action is filed with the Clerk of the Department.

Thank you for applying to the Submerged Lands and Environmental Resource Permit Program. If you have any questions regarding this matter, please contact Heather Mason at (850) 595-0608 or at Heather.Mason@dep.state.fl.us.

Executed in Escambia County, Florida

STATE OF FLORIDA DEPARTMENT
OF ENVIRONMENTAL PROTECTION

Sincerely,

Elizabeth Mullins Orr
Program Administrator
Submerged Lands and Environmental
Resources Program

EO:hm

Enclosures: Section 373.406(6) (1 page)
Drawings (2 pages)

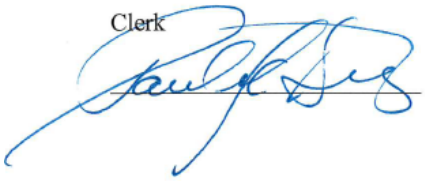
c: USACOE
Doug Fry

CERTIFICATE OF SERVICE

The undersigned duly designated deputy clerk hereby certifies that this exemption, including all copies were mailed and/or emailed before the close of business on MARCH 05, 2013 to the above listed persons.

FILING AND ACKNOWLEDGMENT

FILED, on this date, pursuant to 120.52(7),
Florida Statutes, with the designated Department Clerk,
receipt of which is hereby acknowledged.

Clerk  Date 3/5/2013

Section 373.406(6), Florida Statutes

Any district or the department may exempt from regulation under this part those activities that the district or department determines will have only minimal or insignificant individual or cumulative adverse impacts on the water resources of the district. The district and the department are authorized to determine, on a case-by-case basis, whether a specific activity comes within this exemption. Requests to qualify for this exemption shall be submitted in writing to the district or department, and such activities shall not be commenced without a written determination from the district or department confirming that the activity qualifies for the exemption.

Figure 1. Pinpoint represents the location of the East Dock at USEPA's Gulf Ecology Division research lab in Santa Rosa Sound where the study will take place. (Coordinates provided above).

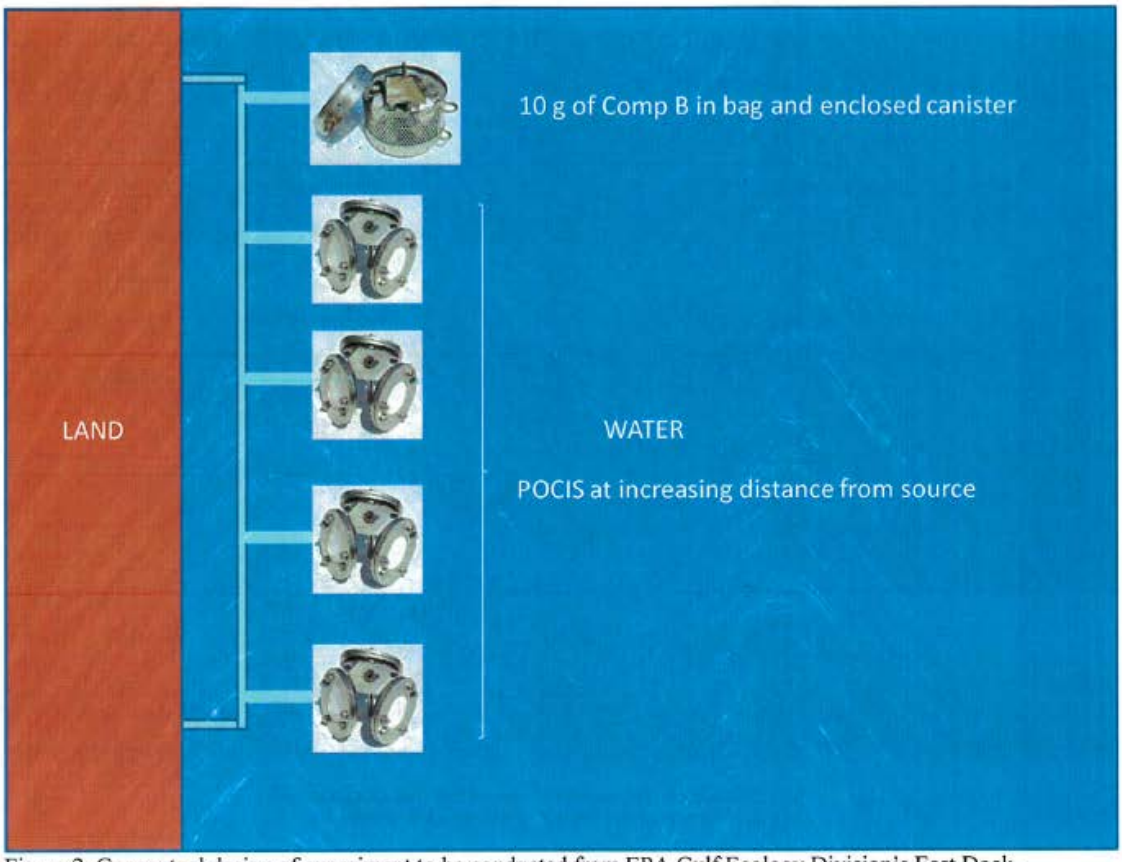


Figure 2. Conceptual design of experiment to be conducted from EPA Gulf Ecology Division's East Dock. Composition B fragment(s) will be placed in bags approximately 1 m below water surface, and secured with appropriate lines to the dock. POCIS passive samplers will be placed at varying distances from the exposure source. All materials will be recovered after approximately 2 weeks.

Figure 3. Commercially available stainless steel canister that will be used to house the POCIS passive samplers. The Composition B fragment will also be contained in one of these canisters and secured to pier with DoD identification tags. http://www.est-lab.com/pocis.php

DEPARTMENT OF THE ARMY
JACKSONVILLE DISTRICT CORPS OF ENGINEERS
PENSACOLA REGULATORY OFFICE
41 NORTH JEFFERSON STREET, SUITE 301
PENSACOLA, FLORIDA 32502

REPLY TO
ATTENTION OF

Regulatory Division
North Permits Branch
Pensacola Permits Section
SAJ-2013-0532 (NW-HMM)

June 6, 2013

US Navy, Space and Naval Warfare Systems Center Pacific, Code 71760
c/o Gunther Rosen
53475 Strothe Road
San Diego, CA 92152

Dear Mr. Rosen:

Your application for a Department of the Army permit received on February 22, 2013, has been assigned number SAJ-2013-0532 (NW-HMM). A review of the information and drawings provided shows the proposed work is to suspend 15 Polar Organic Chemical Integrative Sampler (POCIS) devices (one containing test substance) at varying depths within the water column (ranging from 0.5 to 2.5 meters) along a 60 foot length of the existing dock. The POCIS devices would be suspended from the south side of the dock for 2 weeks and would not touch the bottom substrate. The project is located at the US EPA Gulf Ecology Division Laboratory, at One Sabine Drive, in Santa Rosa Sound, Section 16, Township 3 South, Range 29 West, in Escambia County, Florida.

Your project, as depicted on the enclosed drawings, is authorized by Nationwide Permit (NWP) Number 5. In addition, project specific conditions have been enclosed. This verification is valid until **March 18, 2017**. Please access the U.S. Army Corps of Engineers' (Corps) Jacksonville District's Regulatory Internet page to access Internet links to view the Final Nationwide Permits, Federal Register Vol. 77, dated February 21, 2012, specifically pages 10270 – 10290, the Corrections to the Final Nationwide Permits, Federal Register 77, March 19, 2012, and the List of Regional Conditions. The Internet page address is:

http://www.saj.usace.army.mil/Missions/Regulatory.aspx

Please be aware this Internet address is case sensitive and should be entered as it appears above. Once there you will need to click on "Source Book"; and, then click on "Nationwide Permits." These files contain the description of the Nationwide Permit authorization, the Nationwide Permit general conditions, and the regional conditions, which apply specifically to this verification for this NWP. Enclosed is a list of the six General Conditions, which apply to all Department of the Army authorizations. You must comply with all of the special and general conditions and any project specific condition of this authorization or you may be subject to enforcement action. In the event you have not completed construction of your project within the specified time limit, a separate application or re-verification may be required.

The following special conditions are included with this verification:

1. **Reporting Address:** All reports, documentation, and correspondence required by the conditions of this permit shall be submitted to the following address: U.S. Army Corps of Engineers, Regulatory Division, Enforcement Section, Attention: Terry Wells, 41 North Jefferson Street, Suite 301, Pensacola, FL 32502, or by email at Terry.E.Wells@usace.army.mil. The Permittee shall reference *the above permit number* on all submittals.

2. **Self-Certification:** Within 60 days of completion of the work authorized, the Permittee shall complete the attached "Self-Certification Statement of Compliance" form and submit to the Corps. In the event that the completed work deviates, in any manner, from the authorized work, the Permittee shall describe, on the Self-Certification Form, the deviations between the work authorized by the permit and the work as constructed. Please note that the description of any deviations on the Self-Certification Form does not constitute approval of any deviations by the Corps.

3. **Assurance of Navigation and Maintenance:** The Permittee understands and agrees that, if future operations by the United States require the removal, relocation, or other alteration, of the structures or work herein authorized, or if in the opinion of the Secretary of the Army or his authorized representative, said structure or work shall cause unreasonable obstruction to the free navigation of the navigable waters, the Permittee will be required, upon due notice from the Corps of Engineers, to remove, relocate, or alter the structural work or obstructions caused thereby, without expense to the United States. No claim shall be made against the United States on account of any such removal or alteration.

4. **Regulatory Agency Changes**: Should any other regulatory agency require changes to the work authorized or obligated by this permit, the Permittee is advised that a modification to this permit instrument is required prior to initiation of those changes. It is the Permittee's responsibility to request a modification of this permit from the Pensacola Regulatory Office

5. **Manatee Conditions:** The Permittee shall comply with the attached "Standard Manatee Conditions for In-Water Work – 2011".

6. **Sea Turtle and Smalltooth Sawfish Conditions**: The Permittee shall comply with the attached National Marine Fisheries Service's "Sea Turtle and Smalltooth Sawfish Construction Conditions" dated March 23, 2006, which also applies to Gulf and shortnose sturgeon.

7. No building or fill materials, tools or other equipment shall be stockpiled within the waters of the United States.

8. All contractors involved in this permitted activity shall be provided copies of this permit in its entirety. A copy shall remain on site at all times during construction.

9. **Cultural Resources/Historic Properties:**

   a. No structure or work shall adversely affect impact or disturb properties listed in the *National Register of Historic Places* (NRHP) or those eligible for inclusion in the NRHP.

   b. If during the ground disturbing activities and construction work within the permit area, there are archaeological/cultural materials encountered which were not the subject of a previous cultural resources assessment survey (and which shall include, but not be limited to: pottery, modified shell, flora, fauna, human remains, ceramics, stone tools or metal implements, dugout canoes, evidence of structures or any other physical remains that could be associated with Native American cultures or early colonial or American settlement), the Permittee shall immediately stop all work and ground-disturbing activities within a 100-meter diameter of the discovery and notify the Corps within the same business day (8 hours). The Corps shall then notify the Florida State Historic Preservation Officer (SHPO) and the appropriate Tribal Historic Preservation Officer(s) (THPO(s)) to assess the significance of the discovery and devise appropriate actions.

   c. Additional cultural resources assessments may be required of the permit area in the case of unanticipated discoveries as referenced in accordance with the above Special Condition ; and if deemed necessary by the SHPO, THPO(s), or Corps, in accordance with 36 CFR 800 or 33 CFR 325, Appendix C (5). Based, on the circumstances of the discovery, equity to all parties, and considerations of the public interest, the Corps may modify, suspend or revoke the permit in accordance with 33 CFR Part 325.7. Such activity shall not resume on non-federal lands without written authorization from the SHPO for finds under his or her jurisdiction, and from the Corps.

   d. In the unlikely event that unmarked human remains are identified on non-federal lands, they will be treated in accordance with Section 872.05 Florida Statutes. All work and ground disturbing activities within a 100-meter diameter of the unmarked human remains shall immediately cease and the Permittee shall immediately notify the medical examiner, Corps, and State Archeologist within the same business day (8-hours). The Corps shall then notify the appropriate SHPO and THPO(s). Based, on the circumstances of the discovery, equity to all parties, and considerations of the public interest, the Corps may modify, suspend or revoke the permit in accordance with 33 CFR Part 325.7. Such activity shall not resume without written authorization from the State Archeologist and from the Corps.

This letter of authorization does not give absolute Federal authority to perform the work as specified on your application. The proposed work may be subject to local building restrictions mandated by the National Flood Insurance Program. You should contact your local office that issues building permits to determine if your site is located in a flood-prone area, and if you must comply with the local building requirements mandated by the National Flood Insurance Program.

If you are unable to access the internet or require a hardcopy of any of the conditions, limitations, or expiration date for the above referenced NWP, please contact me by the letterhead address, by email at Holly.M.Millsap@usace.army.mil or by telephone at 850-470-9823.

Thank you for your cooperation with our permit program. The Corps Jacksonville District Regulatory Division is committed to improving service to our customers. We strive to perform our duty

in a friendly and timely manner while working to preserve our environment. We invite you to visit http://per2.nwp.usace.army.mil/survey.html and complete our automated Customer Service Survey. Your input is appreciated – favorable or otherwise. Again, please be aware this Internet address is case sensitive and should be entered as it appears above.

Sincerely,

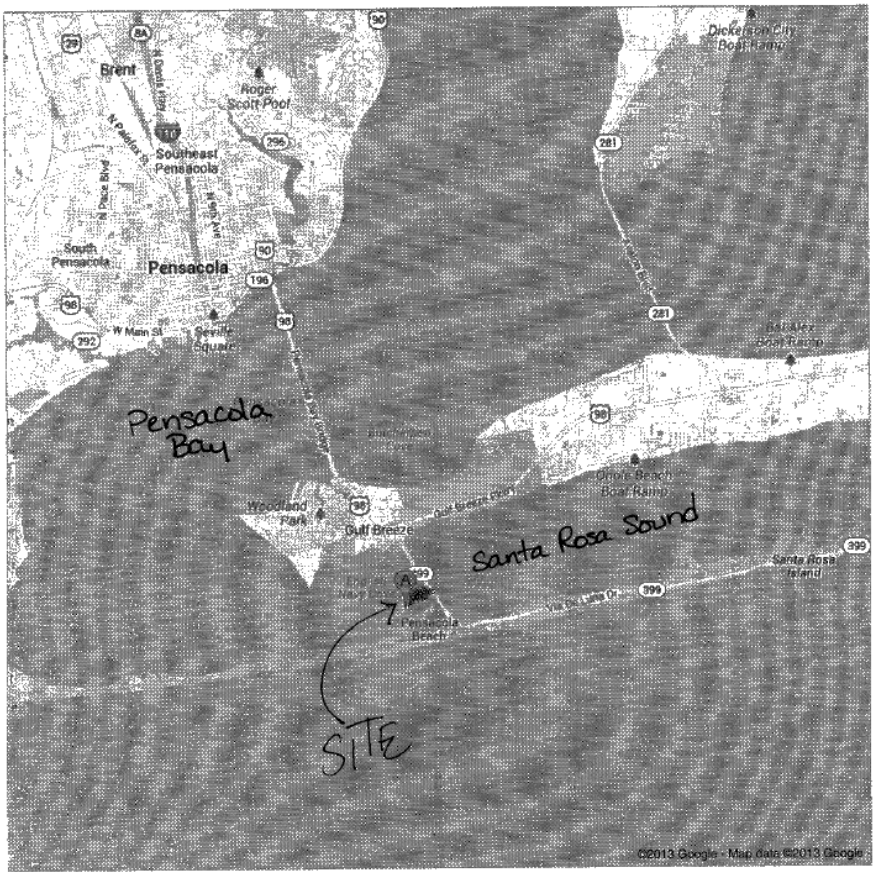
Holly Millsap
Project Manager

Enclosures:
Permit Drawings
General Conditions
Turtle/Sawfish Conditions
Manatee Conditions
Self-Certification Statement of Compliance
Department of the Army Permit Transfer Request

Copy/ies Furnished:
CESAJ-RD-PE

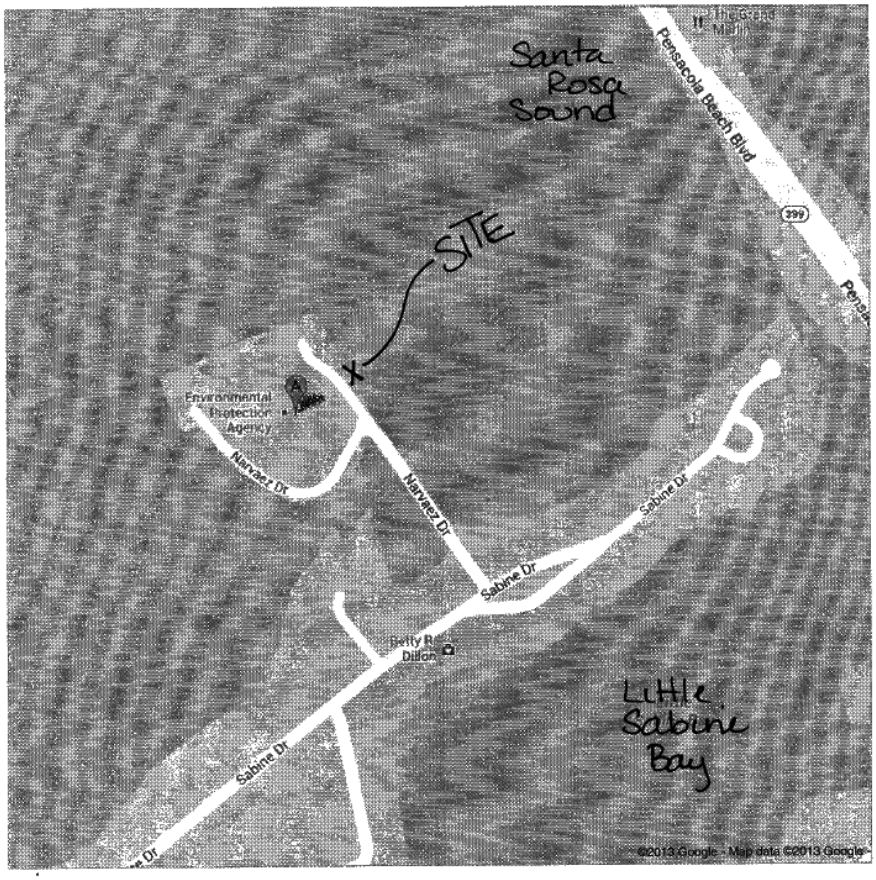
Google

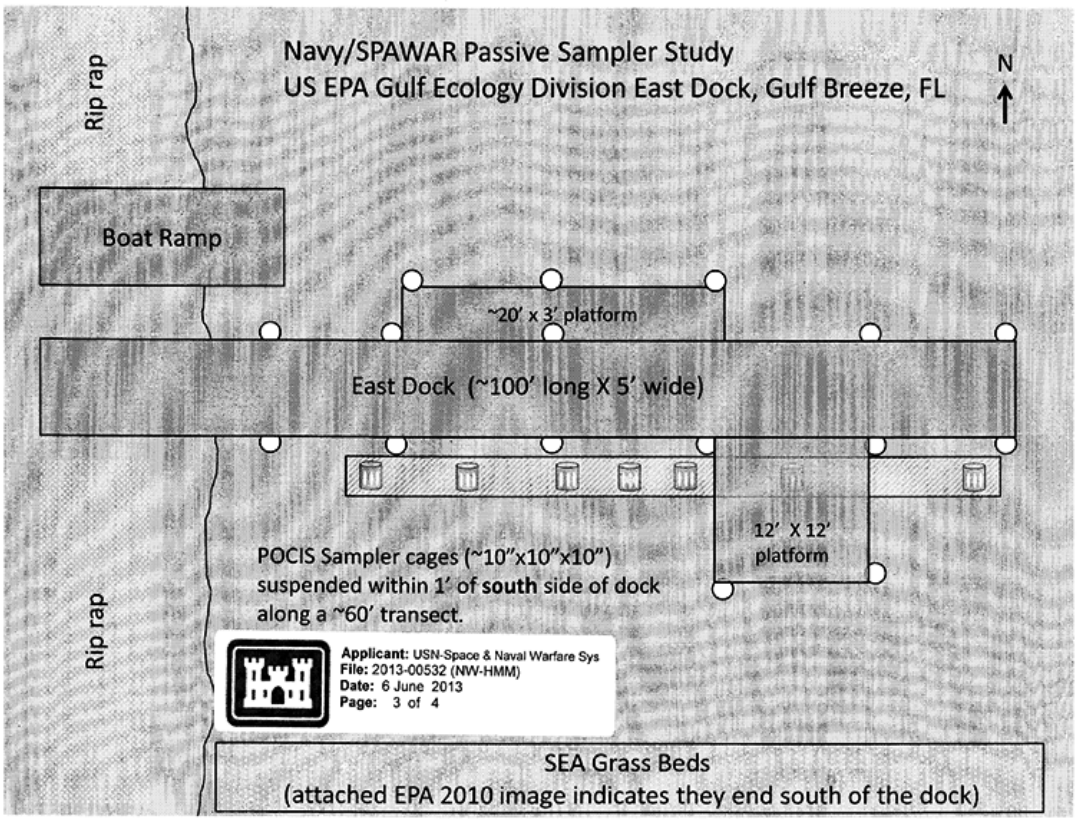
Address **1 Sabine Dr**
Gulf Islands National Seashore,
Gulf Breeze, FL 32561

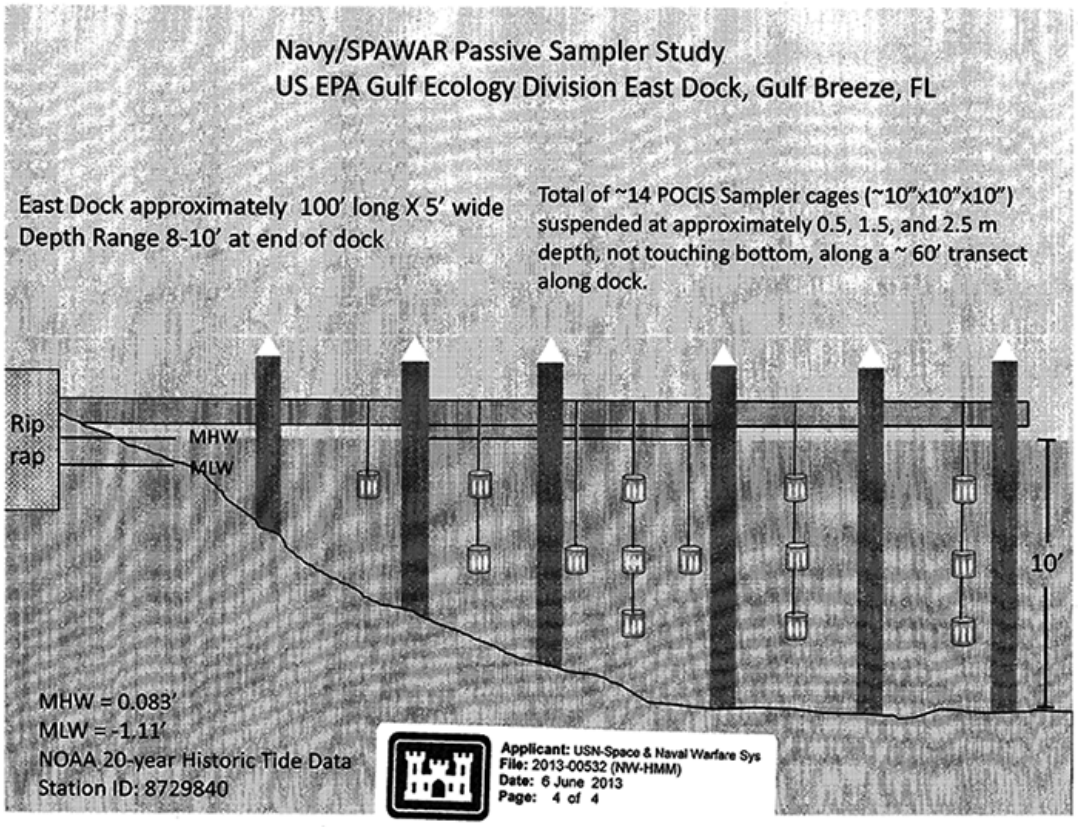


Google

Address **1 Sabine Dr**
Gulf Islands National Seashore,
Gulf Breeze, FL 32561




Navy/SPAWAR Passive Sampler Study
US EPA Gulf Ecology Division East Dock, Gulf Breeze, FL
N
Rip rap
Boat Ramp
~20' x 3' platform
East Dock (~100' long X 5' wide)
12' X 12' platform
POCIS Sampler cages (~10"x10"x10") suspended within 1' of south side of dock along a ~60' transect.
Rip rap
Applicant: USN-Space & Naval Warfare Sys
File: 2013-00532 (NW-HMM)
Date: 6 June 2013
Page: 3 of 4
SEA Grass Beds
(attached EPA 2010 image indicates they end south of the dock)


Navy/SPAWAR Passive Sampler Study
US EPA Gulf Ecology Division East Dock, Gulf Breeze, FL
East Dock approximately 100' long X 5' wide
Depth Range 8-10' at end of dock
Total of ~14 POCIS Sampler cages (~10"x10"x10") suspended at approximately 0.5, 1.5, and 2.5 m depth, not touching bottom, along a ~ 60' transect along dock.
Rip rap
MHW
MLW
10'
MHW = 0.083'
MLW = -1.11'
NOAA 20-year Historic Tide Data
Station ID: 8729840
Applicant: USN-Space & Naval Warfare Sys
File: 2013-00532 (NW-HMM)
Date: 6 June 2013
Page: 4 of 4

GENERAL CONDITIONS
33 CFR PART 320-330
PUBLISHED FEDERAL REGISTER DATED 13 NOVEMBER 1986

1. The time limit for completing the work authorized ends on **date identified in the letter**. If you find that you need more time to complete the authorized activity, submit your request for a time extension to this office for consideration at least one month before the above date is reached.

2. You must maintain the activity authorized by this permit in good condition and in conformance with the terms and conditions of this permit. You are not relieved of this requirement if you abandon the permitted activity, although you may make a good faith transfer to a third party in compliance with General Condition 4 below. Should you wish to cease to maintain the authorized activity or should you desire to abandon it without a good faith transfer, you must obtain a modification of this permit from this office, which may require restoration of the area.

3. If you discover any previously unknown historic or archeological remains while accomplishing the activity authorized by this permit, you must immediately notify this office of what you have found. We will initiate the Federal and state coordination required to determine if the remains warrant a recovery effort of if the site is eligible for listing in the National Register of Historic Places.

4. If you sell the property associated with this permit you must obtain the signature of the new owner in the space provided and forward a copy of the permit to this office to validate the transfer of this authorization.

5. If a conditioned water quality certification has been issued for your project, you must comply with the conditions specified in the certification as special conditions to this permit. For your convenience, a copy of the certification is attached if it contains such conditions.

6. You must allow a representative from this office to inspect the authorized activity at any time deemed necessary to ensure that it is being or has been accomplished in accordance with the terms and conditions of your permit.

UNITED STATES DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
NATIONAL MARINE FISHERIES SERVICE
Southeast Regional Office
263 13th Avenue South
St. Petersburg, FL 33701

SEA TURTLE AND SMALLTOOTH SAWFISH CONSTRUCTION CONDITIONS

The permittee shall comply with the following protected species construction conditions:

a. The permittee shall instruct all personnel associated with the project of the potential presence of these species and the need to avoid collisions with sea turtles and smalltooth sawfish. All construction personnel are responsible for observing water-related activities for the presence of these species.

b. The permittee shall advise all construction personnel that there are civil and criminal penalties for harming, harassing, or killing sea turtles or smalltooth sawfish, which are protected under the Endangered Species Act of 1973.

c. Siltation barriers shall be made of material in which a sea turtle or smalltooth sawfish cannot become entangled, be properly secured, and be regularly monitored to avoid protected species entrapment. Barriers may not block sea turtle or smalltooth sawfish entry to or exit from designated critical habitat without prior agreement from the National Marine Fisheries Service's Protected Resources Division, St. Petersburg, Florida.

d. All vessels associated with the construction project shall operate at "no wake/idle" speeds at all times while in the construction area and while in water depths where the draft of the vessel provides less than a four-foot clearance from the bottom. All vessels will preferentially follow deep-water routes (e.g., marked channels) whenever possible.

e. If a sea turtle or smalltooth sawfish is seen within 100 yards of the active daily construction/dredging operation or vessel movement, all appropriate precautions shall be implemented to ensure its protection. These precautions shall include cessation of operation of any moving equipment closer than 50 feet of a sea turtle or smalltooth sawfish. Operation of any mechanical construction equipment shall cease immediately if a sea turtle or smalltooth sawfish is seen within a 50-ft radius of the equipment. Activities may not resume until the protected species has departed the project area of its own volition.

f. Any collision with and/or injury to a sea turtle or smalltooth sawfish shall be reported immediately to the National Marine Fisheries Service's Protected Resources Division (727-824-5312) and the local authorized sea turtle stranding/rescue organization.

g. Any special construction conditions, required of your specific project, outside these general conditions, if applicable, will be addressed in the primary consultation.

Revised: March 23, 2006
O:\forms\Sea Turtle and Smalltooth Sawfish Construction Conditions.doc

THESE CONDITIONS APPLY TO GULF AND SHORTNOSE STURGEON

STANDARD MANATEE CONDITIONS FOR IN-WATER WORK

2011

The Permittee shall comply with the following conditions intended to protect manatees from direct project effects:

a. All personnel associated with the project shall be instructed about the presence of manatees and manatee speed zones, and the need to avoid collisions with and injury to manatees. The permittee shall advise all construction personnel that there are civil and criminal penalties for harming, harassing, or killing manatees, which are protected under the Marine Mammal Protection Act, the Endangered Species Act, and the Florida Manatee Sanctuary Act.

b. All vessels associated with the construction project shall operate at "Idle Speed/No Wake" at all times while in the immediate area and while in water where the draft of the vessel provides less than a four-foot clearance from the bottom. All vessels will follow routes of deep water whenever possible.

d. All on-site project personnel are responsible for observing water-related activities for the presence of manatee(s). All in-water operations, including vessels, must be shutdown if a manatee(s) comes within 50 feet of the operation. Activities will not resume until the manatee(s) has moved beyond the 50-foot radius of the project operation, or until 30 minutes elapses if the manatee(s) has not reappeared within 50 feet of the operation. Animals must not be herded away or harassed into leaving.

e. Any collision with or injury to a manatee shall be reported immediately to the Florida Fish and Wildlife Conservation Commission (FWC) Hotline at 1-888-404-3922. Collision and/or injury should also be reported to the U.S. Fish and Wildlife Service in Jacksonville (1-904-731-3336) for north Florida or Vero Beach (1-772-562-3909) for south Florida, and emailed to FWC at ImperiledSpecies@myFWC.com.

[Conditions "c" and "f" have been omitted as they are not applicable in Escambia County.]

APPENDIX G
PHOTO-DOCUMENTATION OF POCIS AT VIEQUES

Station T1
Site Location: 256503 E, 2006643 N
Munition Type: MK 82
Munition Condition: Broken open
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians; Porites sp. common at item

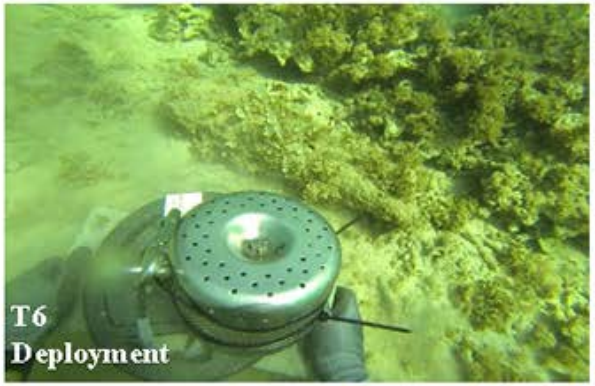
Station T2
Site Location: 256479.72 E, 2006610.96 N
Munition Type: MK 82
Munition Condition: Large Split, low order detonation, at the base
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians

Station T3
Site Location: 256436 E, 2006601 N
Munition Type: MK 82 on top of one 5" round, another 5" round about 6 ft. away. MK-82 likely High Explosive
Munition Condition: Nose sheared, underneath, intact, moderate corrosion
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians

Station T4
Site Location: 256415.05 E, 2006595.16 N
Munition Type: MK 82
Munition Condition: Cut in half, could contain explosives, possible low order
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians
Note: The POCIS sampler fell over during the sampling period, but towards the base of item.

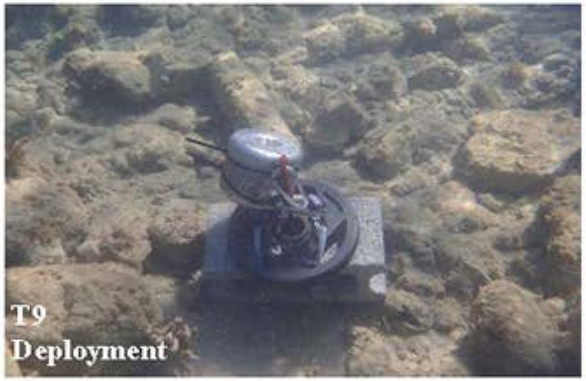
Station T5
Site Location: 256403 E, 2006581 N
Munition Type: MK 82
Munition Condition: Broken open, explosives potentially present, POCIS near the base
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians

Station T6
Site Location: 256388 E, 2006577 N
Munition Type: 5" round
Munition Condition: Broken, split down middle, no fuse visible
Site Description: Colonized bedrock; predominantly macroalgae coverage, with sparse hard coral and gorgonians



Station T7
Site Location: 256878 E, 2006219 N
Munition Type: 5" projectile
Munition Condition: Fused, severe corrosion
Site Description: Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians
Note: POCIS found on side 18" downstream of munition on recovery.

Station T8
Site Location: 256914.76 E, 2006155.09 N
Munition Type: 500 lb. "Old Style" bomb, general purpose
Munition Condition: Fused, moderate corrosion, no tail fin, no crack, intact
Site Description: Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians



Station T9
Site Location: 256926 E, 2006166 N
Munition Type: 5" projectile
Munition Condition: Intact, partial fuse remaining, corrosion
Site Description: Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians

Station T10
Site Location: 256977 E, 2005857.45 N
Munition Type: MK 82, two 3" projectiles nearby
Munition Condition: Fused, severe corrosion, no cracks
Site Description: Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians

Station T11
Site Location: 256986 E, 2005863 N
Munition Type: 16" projectile
Munition Condition: No fuse, cut in half, visible fill material, moderate to severe corrosion, still see rotating bands
Site Description: Colonized bedrock and boulders; sparse coverage of macroalgae, hard coral, and gorgonians

Station T12
Site Location: 256412.228 E, 2005981.216 N
Munition Type: MK 82
Munition Condition: MK 82 LDGP bomb. Nose-up 1/4 proud. 7m deep. Edge seagrass
Site Description: Within edge of sand halo amongst scattered coral/rock; continuous seagrass (90-100%) a northern edge

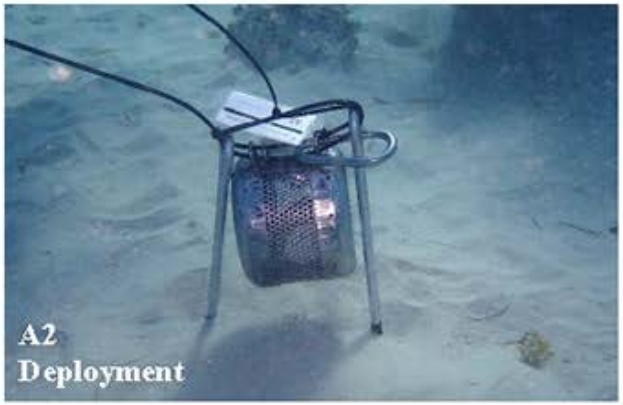
Station T13
Site Location: 256162 E, 2006551 N
Munition Type: 5" projectile
Munition Condition: Intact
Site Description: Colonized bedrock: exposed bedrock contiguous with the shoreline that has coverage of macroalgae, hard coral, and gorgonians

Station T14
Site Location: 256495 E, 2005295 N
Munition Type: 1000lb GP
Munition Condition: Corrosion, visible breach(es)
Site Description: Colonized boulders and bedrock: Patchy coverage of macroalgae and gorgonians, sparse hard corals

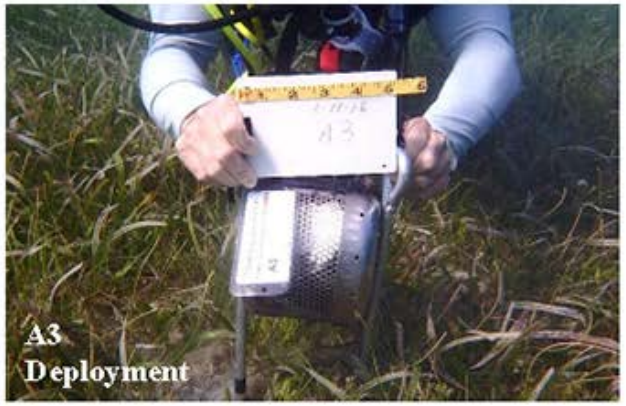
Station T15
Site Location: 256412.228 E, 2005981.216 N
Munition Type: 1000lb GP
Munition Condition: Encrusted with corals, sea fans
Site Description: Colonized Pavement: Flat, low relief, solid carbonate rock and some sand with coverage of macroalgae, hard coral, and gorgonians

Photo documentation of Grid Stations was not made on recovery, but all items were intact, with fouling similar to those observed for Target stations.

Site Location: 255869 E, 2006516 N
Site Description: Within edge of seagrass community (~80% cover); adjacent to large area of mostly bare sand



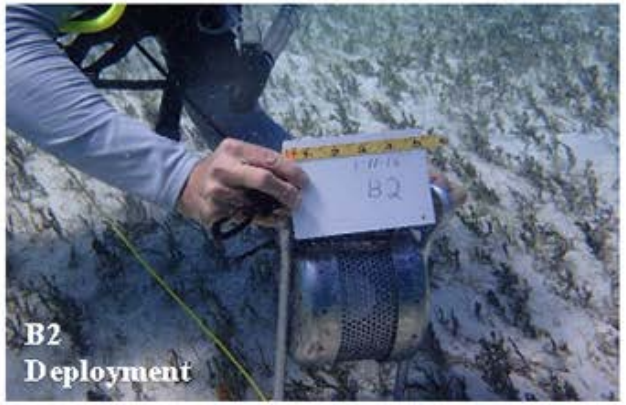
Site Location: 256186 E, 2006552 N
Site Description: Within sand halo at edge of colonized bedrock, as characterized for station T13



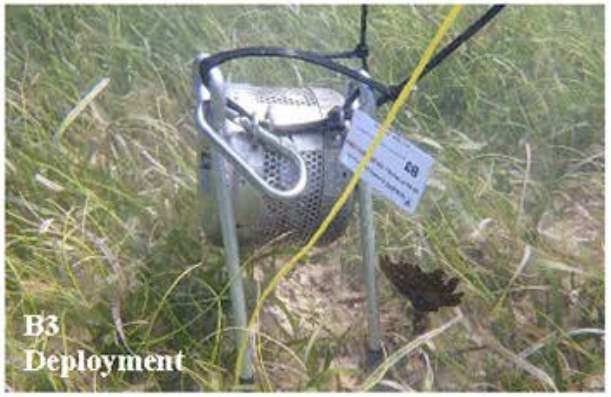
Site Location: 256404 E, 2006505 N
Site Description: Continuous seagrass, 90-100%

Site Location: 256650.26 E, 2006517.15 N
Site Description: Continuous seagrass, 90-100%

Site Location: 255871 E, 2006261 N
Site Description: Continuous seagrass, 90-100%



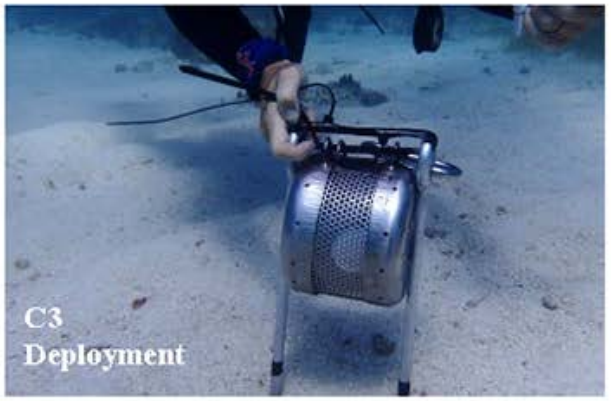
Site Location: 256115 E, 2006505 N
Site Description: Patchy (Discontinuous) Seagrass (50 percent to less than 70 percent cover)



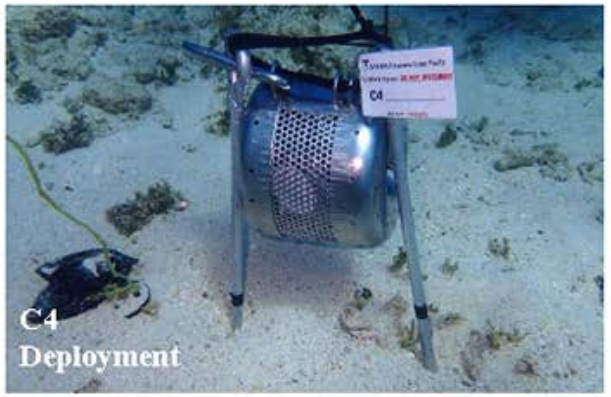
Site Location: 256393 E, 2006252 N
Site Description: Continuous seagrass, 90-100%

Site Location: 256625 E, 2006259 N
Site Description: Continuous seagrass, 90-100%. Good surge, hard pan, difficult to deploy

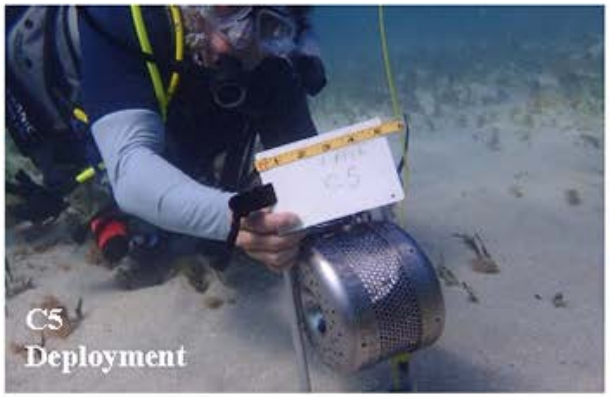
Site Location: 256124 E, 2006003 N
Site Description: Continuous seagrass, 90-100%



Site Location: 256417 E, 2005984 N
Site Description: Within sand halo amongst scattered coral/rock; continuous seagrass (90-100%) immediately north



Site Location: 256650 E, 2006004 N
Site Description: Within sand at eastern edge of colonized pavement: gently sloping carbonate rock with coverage of macroalgae, hard coral, and gorgonians



Site Location: 256913 E, 2005995 N
Site Description: Patchy macroalgae (50-90%) and sand

Site Location: 256387 E, 2005750 N
Site Description: Continuous seagrass, 90-100%

Site Location: 256660 E, 2005750 N
Site Description: In sand patch within colonized pavement: gently sloping carbonate rock with coverage of macroalgae, hard coral, and gorgonians

Site Location: 256916.74 E, 2005745.5 N
Site Description: Sand with patchy macroalgae (~10%), adjacent seagrass areas (50-70%). Hard pack bottom approximately 17" below sand

APPENDIX H
TECHNOLOGY USER'S MANUAL

TECHNOLOGY USER'S MANUAL

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

Environmental Restoration Project #ER-201433

June 30, 2017

Version 1.2

Table of Contents

Acknowledgements

The development of this technology user's guide for integrative passive sampling of munitions constituents was supported by the Department of Defense's Environmental Security Technology Certification Program (ESTCP), project #ER-201433. Leveraged funding was provided by the Navy's Environmental Sustainability Development to Integration (NESDI) program, project #465. The contents of this document build on earlier guidance provided for a wider range of chemicals by the developers of the sampling technology (Alvarez et al. 2010). The ESTCP Final Technical Report for Project ER-201433 (Rosen et al. 2017) was the source of much of the input to the user's guide, and should be consulted as necessary.

1. Acronyms

2,4-DNT	2,4-dinitrotoluene
2,4,6-TNT	2,4,6-trinitrotoluene
2,4-DANT	2,4-diamino-6-Nitrotoluene, aka DANT
2,6-DANT	2,6-diamino-4-Nitrotoluene, aka DANT
2,6-DNT	2,6-dinitrotoluene
2-ADNT	2-amino-4,6-dinitrotoluene, aka 2-ADNT
4-ADNT	4-amino-2,6-dinitrotoluene, aka 4-ADNT
DANT	Diaminonitrotoluene
DoD	Department of Defense
EOD	Explosive Ordnance Disposal
EPA	Environmental Protection Agency
EQL	Environmental Quantitation Limit
ESTCP	Environmental Security Technology Certification Program
GPS	Global Positioning System
HLB	Hydrophilic-lipophilic balance (POCIS sorbent)
IPS	Integrative Passive Sampler
K_{ow}	Octanol-water partition coefficient
LOD	Low Order Detonation
LQL	Laboratory Quantitation Limit
MC	Munitions constituents
MR	Munitions Response
NESDI	Navy's Environmental Security Development to Integration Program
NOSSA	Naval Ordnance Safety and Security Activity
PES	Polyethersulfone
POCIS	Polar Organic Chemical Integrative Sampler
RDX	Hexahydro-1,3,5-trinitro-s-triazine (also Royal Demolition Explosive)
Rs	Sampling Rate
SERDP	Strategic Environmental Research and Development Plan
TNB	1,3,5-trinitrobenzene
TNT	Trinitrotoluene
TWA	Time-weighted average
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UXO	Unexploded ordnance
UWMM	Underwater military munitions

2. POCIS development and description

Traditional water sampling approaches have relied on collection of discrete "grab" samples that represent a single point in time. Despite improvements in technique, such as development of solid-phase extraction (SPE; Buszewski and Szultka, M. 2012), collection of large volumes of water is required to satisfy the detection limit requirements of commonly used analytical methods. In cases where bulk (or filtered) water samples are shipped to the laboratory, the preservation and transport of large volumes of water can be problematic. On the other hand, the use of on-site automated sampling systems can be costly and difficult to maintain (Alvarez et al. 2007). These problems are amplified when the environmental concentrations vary significantly over time and thus numerous timed events are required to be collected to accurately assess concentration.

Environmental contamination of munition constituents (MC) can occur as episodic events including spills, storm water runoff, and varying hydrodynamic and environmental conditions associated with leakage of MC from breached unexploded ordnance (UXO; Wang et al. 2013) or direct exposure associated with low order detonations (LOD). When discrete water samples are only infrequently collected at a site where episodic contamination events are expected, a high probability that contaminants will not be detected exists, especially if the timing of the event is uncertain (Morrison et al. 2016). This problem is particularly relevant to hydrophilic organic compounds, such as TNT, TNT degradation products, and RDX, as their residence times in aquatic systems are generally lower than hydrophobic organic compounds (HOCs). However, transient but frequent occurrence of certain hydrophilic organic compounds in some scenarios may result in temporal changes in receiving water quality. Thus, there is a critical need for sampling and analytical methods capable of enhancing the detection and identification of MC in an integrated manner, which in turn, provides highly relevant time-weighted average (TWA) concentrations. Without this type of methodological advancement, investigators may face a daunting task in adequately assessing the environmental risks posed by this diverse class of chemicals. Achieving a TWA concentration from a single sample can dramatically reduce analytical cost compared to making numerous analytical measurement over a time-course.

Integrative passive samplers (IPS) are samplers for which no significant losses of accumulated residues occur during the exposure period. IPS concentrate ultra-trace to trace levels of chemicals over prolonged sampling periods, generally resulting in greater masses of sequestered chemicals than those recovered using grab sampling techniques. For example, using IPS for trinitrotoluene (TNT) and allowing 14 days of uptake would result in up to 21x more sensitivity. Consequently, the use of IPS is expected to result in increased analytical sensitivity and lower detection limits relative to those reported for most traditional methods. In addition, the use of IPS enhances the probability of the detection of chemicals that rapidly dissipate or degrade. Although a few passive sampling devices have been tested for hydrophilic organic compounds, the first and arguably best studied sampler reported for this chemical class is the polar organic chemical integrative sampler (POCIS), developed by David Alvarez and collaborators at the US Geological Survey, Columbia Environmental Research Center, Columbia, MO (Alvarez 1999; Alvarez et al. 2000).

The POCIS consists of a disk-like configuration of a solid-phase sorbent or a mixture of sorbents sandwiched between two microporous polyethersulfone (PES) membranes. High grade stainless steel rings are used to form a compression seal to prevent sorbent loss, as the PES membrane is not amenable to heat sealing (Alvarez et al. 2004). **Figure 1** depicts an array of POCIS supported on a threaded rod with an exploded view of the "membrane-sorbent-membrane sandwich", which comprises the functional component of the sampler. POCIS are commercially available from EST, Inc. (St. Joseph, Missouri). The compression rings are made of a metallic material and thumb bolts and nuts are used to secure the rings to the membranes. The microporous PES membrane acts as a semipermeable barrier between the sorbent and the surrounding environment. It allows dissolved hydrophilic organic compounds to pass through to the sorbent, while particulates, microorganisms, and macromolecules with cross-sectional diameters greater than 100 nm are selectively excluded. Upon deployment of POCIS, water rapidly permeates the pore structure of PES membrane and makes direct contact with the sorbents. The average thickness of the hydrated PES membrane is approximately 130 µm. For a typical POCIS disk used in field studies, the effective surface area of the membranes in contact with exposure waters is 41 cm^2 and the sorbent mass is ~ 228 mg (Alvarez et al. 2010).

Figure 1. POCIS (top) and commercially available field holder and canister for POCIS (bottom), available from the Environmental Sampling Technologies (EST-Lab.com). Photos from Rosen et al. (2016).

Since their initial development, the use of POCIS as tools for field application have quickly become widespread, including use in large-scale monitoring studies, such as monitoring surface waters of lakes (Li et al. 2010, Sultana et al. 2017) and in rivers in the USA (McCarthy et al. 2007, 2012; Jones-Lepp et al. 2012). Although the majority of the sites investigated using POCIS are rivers, lakes and reservoirs, deployment in marine environments has been increasing (Bargar et al. 2012; Bueno et al. 2009; Harman et al. 2009, 2010, 2011, 2014). Recently, POCIS were also shown to be of high utility for exposure to MC in a marine environment (Rosen et al., 2016; Rosen et al. 2017).

POCIS are designed to sample the more water soluble organic chemicals with log octanol-water partition coefficients (Kow) < 3 (Alvarez et al. 2010). This includes most pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites and degradation products, as well as munitions constituents (MC) such as TNT, RDX and their major transformation products (Belden et al. 2015). **Table 1** lists the MC examined with POCIS to date, and some of their physicochemical characteristics.

Table 1. Physicochemical characteristics of munition constituents that have been studied using integrated passive sampling.

Analyte	Common Referred Name	CAS	Water Solubility, g/L*	Log K_{OW}*
2,4,6 -Trinitrotoluene	TNT	118-96-7	0.13	1.6
2-Amino-4,6-dinitrotoluene	2-ADNT	35572-78-2	0.42	1.94
4-Amino-2,6-dinitrotoluene	4-ADNT	19406-51-0	0.42	1.91
2,4-Diamino-6-nitrotoluene	2,4-DANT	6629-29-4	Not found	0.7
Hexahydro-1,3,5-Trinitro-1,3,5-triazine	RDX	121-82-4	0.56	0.90
1,3,5-Trinitroso-1,3,5-Triazinane	TNX	13980-04-6	73	0.515
2,4-Dinitrotoluene	2,4-DNT	121-14-2	0.27	1.98
2,6-Dinitrotoluene	2,6-DNT	606-20-2	0.21	2.02
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4	0.092	1.16
1,3-Dinitrobenzene	1,3-DNB	99-65-0	0.42	1.58

*Values for TNT, 2-ADNT, 4-ADNT, 2,4-DNT, 2,6-DNT, and RDX obtained from USEPA (2012). Values for TNX, 1,3,5-TNB and 1,3-DNB obtained from Scifinder (http://scifinder.cas.org; accessed 02/03/2017) and calculated using Advanced Chemistry Development Software V11.02 (ACD/Labs). Values for 2,4-DANT from Elovitz and Weber (1999). Conditions were modeled at 25 °C and pH 7.

Munitions have been tested and verified using the standard commercially available POCIS (http://est-lab.com/), which contains the sorbent Oasis® HLB. Oasis® HLB is typically considered a universal sorbent in environmental analyses and has been used to extract a wide assortment of chemical classes from water. The chemical phase of the sorbent (polymeric poly(divinylbenzene-vinylpyrrolidone)) is available from several vendors in the solid-phase extraction (SPE) format, and is frequently used for active extraction of MCs from discrete water samples (DeTata et al 2013; Belden et al. 2015).

3. Theory and modeling

Accumulation of chemicals by IPS generally follows first order kinetics, which is characterized by an initial integrative phase, followed by curvilinear and equilibrium partitioning phases. For all phases of uptake, sampling rates (R_s; units of L day^{-1}) and sorbent-water (sw) partition coefficients (K_{sw}; units of mL mL^{-1} or g^{-1}) are independent of exposure concentrations. During the integrative phase of uptake, a passive sampling device acts as an infinite sink for contaminants, and assuming constant exposure concentrations, residues are accumulated linearly relative to time. POCIS remains in the integrative phase of sampling during exposure periods of at least 30 days for compounds with a log K_{ow} greater than 1 (Alvarez et al. 2010) including many munitions (Belden et al 2015). An advantage of integrative samplers over equilibrium partition samplers is that TWA concentration of contaminants can be determined from sampler concentration data (assuming appropriate calibration data are available). Unlike samplers that rapidly achieve equilibrium (such as those commonly used for hydrophobic compounds such as

PAHs and PCBs), chemical residues from episodic release events are retained by integrative samplers at the end of the exposure period. Thus, integrative samplers have very small analyte loss rates and times to reach equilibrium are very large for most compounds evaluated (Alvarez et al. 2010).

Estimates of ambient environmental concentrations of analytes from the concentrations in a passive sampler can be made for most munitions as previous research has demonstrated that accumulation in the POCIS is proportional to environmental concentrations across environmentally relevant concentrations. In order to calculate environmental concentrations, the rate at which the analyte partitions from water to the POCIS must be experimentally determined for a given set of environmental conditions. These rates are relatively stable across temperature and salinity; however, adjustment may need to be made based on changes in flow across the sampler. The following equation for integrative (i.e., linear) sampling by an IPS:

$$C_w = \frac{N}{R_s t}$$ Equation 1

In this equation, N is the amount of the chemical accumulated by the sampler (ng), R_s is the sampling rate (L day^{-1}), and t is the exposure time (day).

The POCIS is well-suited as a screening tool for determining the presence or absence of, sources, and relative amounts of chemicals at study sites, but the reasonable estimation of ambient water TWA concentrations requires knowledge of the sampling rate for each chemical measured. Recent studies have involved calculation of rates for many MC (**Table 2**).

4. Advantages and limitations compared to other sampling techniques

POCIS provides a means for determining the TWA concentrations of targeted chemicals that can be used in risk assessments to determine the biological impact of hydrophilic organic compounds on the health of the impacted ecosystem. Generating a sufficient number of samples to estimate TWA concentration by traditional methods may be logistically and financially imprudent as part of a regular monitoring program. Field studies have shown that POCIS has advantages over traditional sampling methods in sequestering and concentrating ultra-trace to trace levels of chemicals over time resulting in increased method sensitivity, ability to detect chemicals with a relatively short residence time or variable concentrations in the water (i.e., chemical/biological degradation, sorption, dissipation), and simplicity in use. POCIS has been successfully used worldwide under various field conditions ranging from stagnant ponds to shallow creeks to major river systems in both fresh and brackish water. Due to the quality of the data obtained, ease of use, and broad applicability to both chemical and biological assessments, the POCIS technique has the potential to become the standard for global water quality monitoring for munitions.

POCIS are designed to be relatively long-term (i.e. 2-4 week) integrative samplers. Generally, these samplers will provide little benefit over traditional discrete (grab) samples for study periods less than 5-7 days. Integration occurs over an extended time frame and shorter time

Table 2. Compilation of all known studies conducted for MC sampling rates.

Analyte Name (common abbreviation)	CAS number	Sampling Rate Studies, mL/d	Study
2,4,6-Trinitrotoluene (TNT)	118-96-7	93±13, ~0.1cm/s; 25°C, salinity of 30 g/L	1
		Uncaged rate=81(flow rate)+14; caged rate=18(flow rate)-50	2
		125±18, ~0.1cm/s; 25°C, salinity of 30 g/L	3
		97±16, static, 440±96 high flow; 23°C, salinity of 30 g/L	4
4-Amino-2,6-dinitrotoluene (4-ADNT)	19406-51-0	104±19, ~0.1cm/s, 25°C, salinity of 30 g/L	1
		81±17, static, 324±69 high flow; 23°C, salinity of 30 g/L	4
2-Amino-4,6-dinitrotoluene (2-ADNT)	35572-78-2	97±21, ~0.1cm/s, 25°C, salinity of 30 g/L	1
		111±24, static, 474±114 high flow; 23°C, salinity of 30 g/L	4
2,4-Diamino-6-nitrotoluene (DANT)	6629-29-4	34±4, ~0.1cm/s, 25°C, salinity of 30 g/L*	1
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	Rs (up to 14 days) - 129±29, equilibrium (longer than 28days) 16400ml/g (HLB/water), ~0.1cm/s, 25°C, salinity of 30 g/L;	1
		Uncaged rate=5(flow rate)+0314; caged rate=8(flow rate)+270	2
		493±116, ~0.1cm/s; 25°C, salinity of 30 g/L	3
		229±44, static, 515±170 high flow; 23°C, salinity of 30 g/L	4
2,4-Dinitrotoluene (2,4-DNT)	121-14-2	Uncaged rate=3(flow rate)+52; caged rate=4(flow rate)+80	2
		82±6, ~0.1cm/s; 25°C, salinity of 30 g/L	3
		50±9, static, 272±32 high flow; 23°C, salinity of 30 g/L	4
2,6-Dinitrotoluene (2,6-DNT)	606-20-2	Uncaged rate=3(flow rate)+65; caged rate=4(flow rate)+7	2
		85±13, static, 359±63 high flow; 23°C, salinity of 30 g/L	4
3,5-Dinitroaniline (3,5-DNAL)	618-87-1	50±14, static, 339±106 high flow; 23°C, salinity of 30 g/L	4
1,3,5-Trinitrobenzene (TNB)	99-35-4	77±8, static, 329±56 high flow; 23°C, salinity of 30 g/L	4
1,3-Dinitrobenzene (DNB)	99-65-0	45±4, static, 274±32 high flow; 23°C, salinity of 30 g/L	4
Hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)	3980–04-6	No R_s can be calculated. Equilibrium (longer than 6 days) 6180 ml/g (HLB/water), ~0.1cm/s, 25°C, salinity of 30 g/L	1

1. Belden et al. 2015; 2. Lotufo et al., in preparation; 3. Rosen et al., in preparation; 4. Belden et al., in preparation.

periods may suffer quantitatively from a lag effect. Time periods long than 21-28 days may also be avoided as the integrative period may be exceeded, along with increased risk associated with other field deployed devices including fouling, damage, and/or loss.

An advantage of using an integrative sampler such as POCIS is that episodic events (e.g. surface runoff, spills, and other unpredictable sources of contamination) can be sampled without the cost and challenges of trying to capture these events with trained staff at potentially remote locations; however, because of the sampling nature of the devices, it is generally unlikely to determine when the event occurred during the exposure period, or know the maximum concentration of a chemical related to the event. Integrative samplers provide data as TWA concentration of a chemical within the whole exposure period. In general, an integrative assessment such as that collected by a POCIS will be more accurate to toxicologically relevant exposure as compared to infrequent collection of discrete samples (Morrison et al. 2016).

5. Commercial availability

POCIS are commercially available from Environmental Sampling Technologies Inc (EST, St. Joseph, Missouri; http://est-lab.com; **Figure 1**). POCIS technology, covering manufacture and assembly, is the subject of US Government patent (#6,478,961 B2) that is licensed to EST. The patent does not cover the extraction processing of the samples, however, extraction service is offered by EST.

Deployment canisters are commonly used to protect the passive samplers in the field (**Figure 1**). Canisters are commercially available from EST and hold three- or six-POCIS assembled to a holder that is secured inside the canister (**Figure 1**). The canisters are made of 304 stainless steel mesh body with perforated 304 SS lid and bottom and are designed to protect the passive samplers from damage and allow adequate water movement through the canister. Openings in the canister are small enough to prevent large debris or organisms from entering the canister which may damage the passive samplers. Recent POCIS prices and corresponding deployment devices provided by EST are shown in Table 3. EST also rents canisters and holders for samplers, if desired.

Table 3. Recent POCIS and corresponding deployment device pricing from EST (EST-Lab.com)

Product	Unit price
POCIS (single sampler)	$65
POCIS Holder (up to three samplers)	$68
Small Canister w/ POCIS Holder (for 3 samplers)	$351
Large Canister w/ 2 POCIS Holders (for 6 samplers)	$531
Sample extraction service (each)	$50

6. Planning and preparation for field sampling

The recommended POCIS exposure duration for MC is 14-21 days (Belden et al. 2015; Rosen et al. 2017). The actual underwater deployment time in the field must be documented. Shorter

deployment times should be contemplated if required by logistical constraints, but deployment time longer than three weeks is discouraged.

The analytical requirements of the study will dictate the number of passive samplers needed. Because the amount of chemical sampled is directly related to the surface area of the device, it is sometimes necessary or desirable to combine the extracts from the sorbents of multiple POCIS disks into a single sample to increase the mass of sequestered chemical for analysis. Knowledge of the mass of a chemical, total number of nanograms (ng) for example, which must be sampled to meet the detection criteria of the chemical analysis will affect the study design. The number of samplers needed as related to the desired environmental quantitation limit can be estimated using the following equation (Equation 2):

$$EQL = \frac{LQL \times V}{n \times R_S \times t}, \qquad \text{Equation 2}$$

Where, EQL is the quantitation limit in terms of the environmental water concentration (ng/L); LQL is the laboratory quantitation limit in terms of concentration in the extract (ng/L); V is the volume of the laboratory extract (ml); n is the number of POCIS combined; R_s is the sampling rate for the analyte of interest into POCIS (L/d); and t is time in days.

Based on the LQL obtained from the analytical laboratory, the number of samplers and enrichment (final laboratory extract volume obtained through solvent evaporation) can be determined that will allow the required EQL to be reached. Typical values for V are 0.5-5 ml and typical number of POCIS is 1 or 3.

Due to the assumption that relatively few munitions will be leaking at any given time at a given UWMM site, compositing three for each sample and reduction of extract volume to 1 ml by the analytical laboratory is recommended. Additionally, LQL will vary based on the laboratory methodology that is conducted. In a recent controlled field validation study using 15 g sample of Composition B fragments (representing leaking UXO) as a point source, method quantitation limits as low as 2 ng/L were achieved when three composited POCIS were extracted at each sampling location (Rosen et al. 2017). For comparison, if an analytical laboratory is able to provide an EQL for MC of 100 ng/L based on a 1L water sample, the three POCIS deployed for 14 days for TNT would result in a EQL of 22.7 ng/L ((100ng/ml x 1 ml)/(3 x 0.105 L/d x 14d)).

The passive samplers should be transported to the field in clean airtight metal cans on blue or wet ice. This is most easily done directly by the manufacturer. If wet ice is used, it should be placed in plastic Ziploc bags to help prevent leaking which could result in the metal shipping cans rusting. It is important that the cans are not opened before use to prevent potential contamination from airborne chemicals. The cans containing the samplers should preferably be stored at <0 °C or at a minimum, kept cool (< 4 °C).

Figure 2 illustrates the preparation of commercially available samplers prior to field deployment. Samplers are shipped by the vendor to the site in a solvent rinsed paint can, in stacks of up to 12 samplers per can. On the day of the field deployment, the samplers are removed from the can, and attached to the available POCIS holder with stainless steel nuts and

bolts (also available from the vendor). The POCIS holder is then placed onto a center post on the field canister and the accompanying lid is screwed on tight. The sampling canister is then packed in a large Ziploc bag and placed into an ice chest on blue ice to keep at 4 °C during transport to the field site.

Remove samplers from freezer and storage canister | Hand tighten samplers to POCIS holder with stainless steel screws | Place holder on deployment canister post | Screw lid on to field canister | Store cold during transport to field site

Figure 2. Pictorial of assembly of POCIS samplers in preparation for field deployment.

7. Quality Control in the Field

Field blanks are POCIS stored in airtight containers and are transported to the field sites in insulated containers filled with blue ice or wet ice sealed in plastic bags. During the deployment and retrieval operations (the time the field passive samplers are exposed to air), the lids to the field blank containers are opened allowing exposure to the surrounding air. Field blanks account for contamination during transport to and from study sites, exposure to airborne contaminants during the deployment and retrieval periods, and from storage, processing and analysis.

8. Compliance with Safety at DoD Munitions Response Sites

The conduct of field studies at UWMM sites is likely to require significant planning to ensure that the work is conducted safely and in compliance with multiple regulatory requirements. This is particularly important at Department of Defense (DoD) munitions response (MR) sites where strict compliance with the Naval Ordnance Safety and Security Activity (NOSSA) and/or other regulatory authorities may be required. It is likely that at such sites, an Explosives Safety Submission (ESS) Determination Request (DR) will need to be requested and approved by appropriate staff. A Dive Safety Plan will also likely be required for approval by appropriate authorities, and Explosive Ordnance Disposal (EOD) technicians and/or munitions response (MR) divers might be required on site depending on the sampling design.

9. Field deployment

A thorough cleaning of the deployment canisters before loading with the passive samplers is critical. Cleaning methods may involve a dilute acid wash (to remove salts and loosen surficial sediments and biological growth), hot soapy water wash, tap or deionized water wash, and

finally an organic solvent rinse starting with a polar solvent (isopropanol alcohol or acetone) followed by a nonpolar solvent (hexane), per recommendations by Alvarez et al. (2010)

The types of equipment required for the deployment and retrieval of passive samplers can vary depending on the site and how the samplers are deployed. This is particularly important at Department of Defense (DoD) munitions response (MR) sites where strict compliance with the Naval Ordnance Safety and Security Activity (NOSSA) and other regulatory authorities may be required. It is likely that at such sites, Navy Explosive Ordnance Disposal (EOD) technicians, and trained divers trained for safely conducting fieldwork at MR sites will be required. General equipment needs are listed below:

- Ice chest/cooler for transporting the passive samplers to/from the field
- Blue ice or wet ice (sealed in plastic bags)
- Canister(s) in sealed metal cans
- Trip/field blank(s)
- Assorted tools (wrenches, pliers, cutters, saws)
- Appropriate water quality logging devices (e.g. temperature, salinity/conductivity)
- Current profiler (e.g. Nortek) to continuously log flow velocity and direction
- Weighted anchoring system or sand screws
- Signage, markings (depending on site vandalism potential)
- Field log book/sheets, digital camera
- Additional requirements associated with MR and scientific diver needs

It is favorable to have the samplers in areas with flow, as the volume of water sampled per day (sampling rate, R_s) generally increases with current velocity (**Table 2, 4**). This said, higher current velocities may also result in accelerated dilution from MC sources. The appropriate R_s should be selected according to concurrently measured, or at least historical, on site-average current velocities. Incorporation of micro-flow sensors (being evaluated under SERDP project #ER-2542) into the canister would provide enhancement of the quantitative estimation of the TWA concentration.

Of additional critical importance to site selection is that the POCIS remain submerged throughout the deployment period. Exposure to air for many weakly hydrophobic and polar organics is of substantial sig nificance, but this is merely a precaution for UWMM, as exposure to air during deployments for MC appear to be of relatively low risk.

10. Deployment Options

1. **From shoreline**: POCIS canisters can be placed in shallow locations near shorelines by wading, or by suspending from piers or docks. Because canisters are negatively buoyant, and can be further weighted, suspension to relatively large depths is feasible. With respect to MC, POCIS would ideally be deployed in the vicinity of known munitions that are potentially leaking MC for conservative assessment. It should be noted that considerable resources to identify leaking munitions are required and can substantially affect sampling costs. The deployment approach used to demonstrate the sensitivity of POCIS positioned around a known quantity of the explosive fill Composition B (59.5%

RDX, 39.5% TNT, 1% wax) involved suspension of samplers off of a dock (**Figure 3**), which could be replicated in locations where such structures are available, eliminating the need for costly dive support.

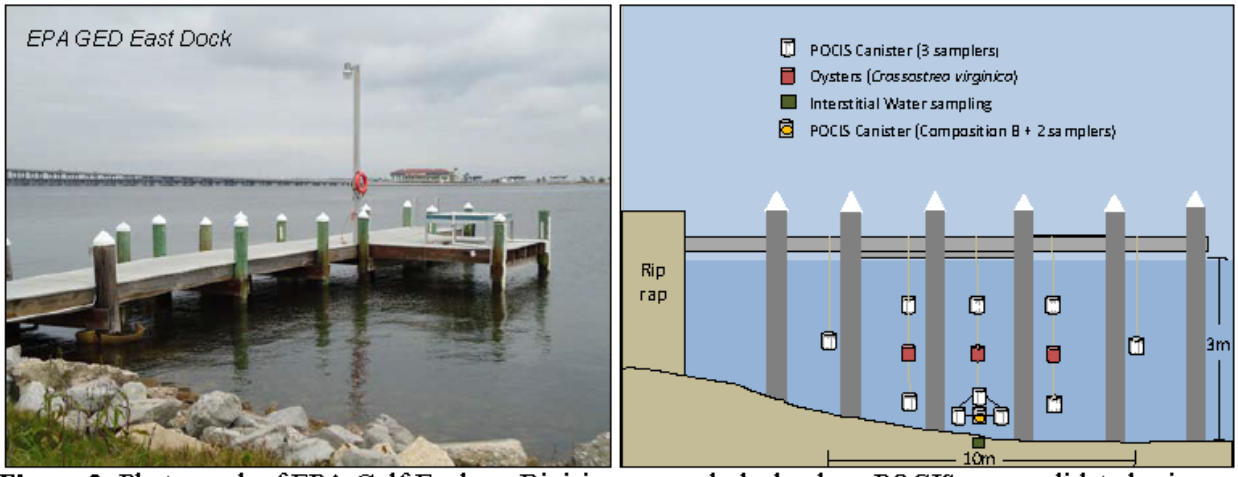


Figure 3. Photograph of EPA Gulf Ecology Division research dock where POCIS were validated using the Composition B (left); underwater representation of POCIS deployment under the EPA dock. **Note**: the number and placement of samplers were for validation purposes, and not necessarily a recommendation for regulatory monitoring around a given munition/source.

2. **From boat by divers:** Boats are often necessary to reach sites in large bodies of water, and may be particularly important at DoD UWMM sites. Deployment canisters can be suspended off the bottom by attachment to piers, pilings, floating platforms, buoys, or other structures. Alternatively, canisters can be suspended from the bottom using sand screws or other anchoring systems (e.g. **Figures 4 and 5**). Divers, guided by document Global Positioning System (GPS) coordinates, or by surface markers, may be required to retrieve canisters not secured to surface structures. However, the potential for vandalism at some sites may reduce feasibility of using surface markers at some sites. If GPS coordinates are not available, use of terrestrial-based reference points may be useful for marking and retrieval efforts.

3. **From boat with mooring:** A mooring, or permanent structure placed in proximity to UWMM (on biased or unbiased bases), may be used to maintain POCIS at UWMM sites during the exposure period (**Figure 4**), with relatively limited concerns regarding vandalism and diver costs. In some cases, attachment of POCIS to moorings may be practical from a survey vessel without the need for MR diver support.

Figure 4. Deployment options for POCIS at a UWMM site including (left) screw anchors holding a POCIS sampler in place above sea floor using a grid (non-biased) deployment option; (center) placement of POCIS on a weighted brick system near potential leaking UWMM; or (right) using a mooring system in water column, potentially eliminating the requirement for cost and safety factors associated with munitions response divers.

(1) Munition screening with a magnetometer, followed by placement of sand screws for POCIS placement 12" above sea floor.

(2) POCIS placed above sediment following screening for munitions presence at a non-target station location.

(3) Preparation of a POCIS sampler on weighted block system for placement <12" from a potentially leaking munition.

(4) Munitions response divers using a lift bag to place a weighted-POCIS sampler near a potentially leaking munition.

(5) Close up view of a weighted POCIS sampler <12" from a potentially leaking munition.

Figure 5. Use of magnetometer followed by anchoring of POCIS canisters with sand screws (1 and 2); preparation of a POCIS weighted anchoring system, transport to the station with a lift bag, and placement adjacent to a munition (3-5).

11. Vertical Gradients

Depending on the depth of the water body, substantial gradients in the concentrations of contaminants can occur with depth. Seasonal differences in water temperature, density, and potential inputs such as effluent streams can all affect where in the water column the highest concentrations of contaminants may occur. To study this, samplers can be placed at various depths. In the case of MC, it is likely that the highest concentrations in an open water body

would be within immediate proximity (i.e. inches to a few feet) from breach munitions. The placement of samplers should be based on specific objectives of the study.

12. Biological Growth

In brackish and marine waters, a buildup of hard biofouling (e.g. barnacles) or micro- or macro-algae may occur, reducing sampling rate by POCIS. Predicting when a buildup of organisms may occur can be difficult in most brackish and marine deployments. A high degree of biofouling may make it difficult to remove the samplers, or to expect realistic sampling of available MC. If biological growth is a concern at the site, exposures should be limited to 14 days to reduce impacts on sampling rate and potentially reduced rate of uptake of target contaminants by the POCIS (**Figure 6**; Rosen et al. 2017).

Figure 6. Examples of biofouling on POCIS after (left to right), 0, 7, 14, and 28 d of field deployment at an estuarine site (Rosen et al. 2017).

13. Hardware

Many options exist for the types of hardware that can be used for securing the canisters during field deployment. Strength and protection from vandalism should be considered when selecting materials. Stainless steel (SS) hardware is preferred for prolonged water exposure and is required in marine environments to prevent corrosion. SS carabiners are recommended for securing the canisters to surface or weighted support structures, such as those shown in **Figure 4**. The hardware should be thoroughly cleaned before use with organic solvents such as acetone or hexane to remove any residual surfactants from detergent-based cleaning. Large nylon cable ties, heavy duty carabiners, or a combination of the two, can be used to secure canisters at specific locations, depending on the deployment strategy.

14. Field Observations and Measurements

Physical and chemical characteristics associated with deployment sites can be useful in the estimation of ambient concentrations and the final interpretation of the data. Water temperature, pH, conductivity, current velocity, and at least visual assessment of biofouling should be documented. Current velocity may have two-fold, or more, effect on estimation of TWA concentrations. By incorporation of current meters into the field deployment, current velocity can

be used to select the most appropriate sampling rate based on regression equations that have been derived for multiple MC (**Table 4**; Lotufo et al., in prep; Rosen et al. 2017).

General observations that can be useful for anchoring and data interpretation, as identified by (Alvarez et al. 2010) include:

- Bottom conditions (soft, rocky)
- Water conditions (clear/murky, suspended sediment levels, surface film, algal growth)
- Weather/air quality during field work
- Water temperature (Harman et al. 2011)
- Condition of the samplers when retrieved

Water temperature and salinity should be measured at the beginning and end of the deployment at minimum. Monitoring of water temperature and salinity using commercially available data loggers (e.g. Onset Corp, HOBO®) attached to or in the proximity of the deployment canisters is preferable. Other water properties such as pH, suspended solids concentrations, dissolved organic carbon, may be useful when discussing chemical speciation, distribution, and fate, but are generally not collected as part of a passive sampler study (Alvarez et al. 2010).

Table 4. Suggested sampling rates for common conventional munitions constituents based on quantified or estimated flow velocity at site.

Analyte Name (common abbreviation)	CAS number	Sampling Rate Studies, mL/d	Quantitative Certainty
2,4,6-Trinitrotoluene (TNT)	118-96-7	<9 cm/s flow = 105 9-30 cm/s flow = 18(flow rate)-50 >30 cm/s flow = 490	High
4-Amino-2,6-dinitrotoluene (4-ADNT)	19406-51-0	< 10 cm/s = 92.5 >10 cm/s = 324	Moderate
2-Amino-4,6-dinitrotoluene (2-ADNT)	35572-78-2	< 10cm/s = 104 >10 cm/s = 474	Moderate
2,4-Diamino-6-nitrotoluene (2,4-DANT)	6629-29-4	All flows= 34	Low
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	<7 cm/s flow = 284 7-30 cm/s flow = 8(flow rate)+270 >30 cm/s flow = 510 If longer than 21 day exposure (equilibrium) = 16400ml/g (HLB/water)	High – less than 14 days suggested
2,4-Dinitrotoluene (2,4-DNT)	121-14-2	<7 cm/s flow = 66.3 7-30 cm/s flow = 4(flow rate) + 80 >30 cm/s flow = 200	High
2,6-Dinitrotoluene (2,6-DNT)	606-20-2	<20 cm/s flow = 85 20-30 cm/s flow = 4(flow rate) + 7 >30 cm/s flow = 127	High
3,5-Dinitroaniline (3,5-DNALIN)	618-87-1	< 10cm/s = 50 >10 cm/s = 339	Low
1,3,5-Trinitrobenzene (TNB)	99-35-4	< 10cm/s = 77 >10 cm/s = 329	Low
1,3-Dinitrobenzene (DNB)	99-65-0	< 10cm/s = 45 >10 cm/s = 274	Low
Hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)	3980–04-6	Equilibrium constant valid if longer than 6 days = 6180 ml/g (HLB/water)	Low

Higher – indicates replicated studies with commercial POCIS and consideration of flow.
Moderate – indicates replicated studies with at least some work with commercial samplers and some consideration of flow.
Low – Operation only as an equilibrium sampler, no replication, no consideration of flow, or no measurements with commercial samplers.

15. Shipment, Storage, and Recovery

Following recovery of the samplers, and verification of their condition post deployment, the samplers can be shipped intact in the field canisters placed in large Ziploc bags. Alternatively, individual POCIS should be removed from the field canister, and be individually packed in small Ziploc bags and then with bubble wrap to reduce likelihood for membrane puncture during shipment (**Figure** 7). During on-site storage, recovered samplers should be kept frozen.

Samplers should be shipped overnight on blue or wet ice at < 4°C to the analytical laboratory. Dry ice should not be used as it can damage the passive samplers.

Visual inspection for damage or biofouling

Removing POCIS from field canister

Individual sampler preservation/bagging to prevent contamination

Bubble wrap and shipment at 4°C to prevent damage

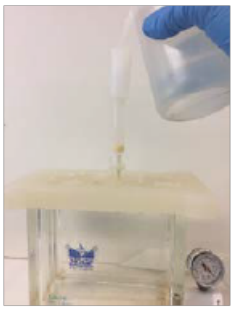
Figure 7. Upon recovery, samplers are inspected for damage and biofouling, carefully removed from the field canister, photo-documented, and individually wrapped in labeled Ziploc bags. Prior to shipment, each bag is wrapped in bubble wrap to minimize risk of membrane damage during transport.

16. Processing of the POCIS

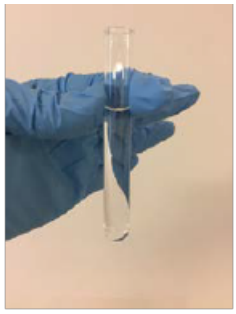
The first step in chemical analysis is to perform an extraction procedure for the POCIS. The extraction methods for the recovery of chemicals from the POCIS typically conducted with MC involves opening the POCIS, rinsing the sorbent into an empty SPE tube, and then eluting with solvent that is captured and evaporated to a small known volume (**Figure 8**). It is recommended that large empty cartridges with capacities of 15 mL or greater be used, or alternatively 6-ml SPE tubes, and a tight-sealing reservoir is placed on top to allow for adequate volumes of rinse and elution solvent (**Figure 9**). Prior to rinsing the sample into the column, a frit is placed in the bottom of the SPE cartridge (Oasis HLB sorbent).

The cartridge and frit are rinsed with the solvents to be used during the POCIS extraction and dried. The flow of solvent and water through the cartridge can be achieved using a vacuum manifold (**Figure 9**). The POCIS is opened over a funnel and ultrapure water is used to transfer the sorbent into the cartridge. The water does not need to be retained. The sorbent is dried by vacuum to remove all traces of water before extraction. Elution of analytes can be conducted by several solvents (DeTata et al. 2013). Although POCIS extraction has been recommended to use 40 ml of methanol, smaller volumes of ethyl acetate and acetonitrile (10 ml recommended) have been shown to readily extract MC from the small mass of sorbent recovered from a single POCIS (DeTata et al. 2013, Belden et al. 2015).

POCIS are dismantled either by removing bolts or by using a sharp knife to cut the membrane. The stainless steel knife and aluminum foil used to catch any leaked material should be solvent washed.



The sorbent contained in the POCIS is carefully transferred into an empty solid-phase extraction (SPE) tube that contains a frit. The tube and frit must be cleaned/new and solvent washed prior to use. Water and vacuum can be used to collect all sorbent against the frit. The water is discarded and the vacuum is pull for a few minutes to dry the sorbent.



A test tube is then placed under the SPE tube. Analytes on the sorbent are eluted using solvent and collected in the test tube. The volume of the solvent can then be reduced under a stream of nitrogen to allow for an accurate final volume and enrichment of the sample.

Figure 8. Steps required to remove sorbent from POCIS sampler, collect sorbent on SPE tubes, and elute the analytes into a test tube for analysis.

For GC analysis, ethyl acetate is recommended as drying of the solvent with anhydrous sodium sulfate and evaporation is quicker. For LC analysis, laboratories may choose acetonitrile to limit the need for solvent exchange. For MC analyses, evaporation to dryness should be avoided. Note: this process is analogous to the final steps of analysis using SPE extraction. If a laboratory has an SPE extraction analysis, their current procedures can be used once the sorbent is rinsed into the SPE column. Once the extract is obtained, analysis can be performed using any methodology accepted for MC analysis (e.g. EPA 8330, EPA 8095).

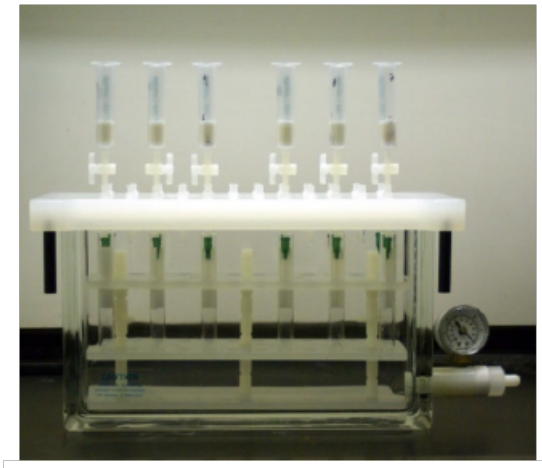


Figure 9. POCIS extraction vacuum manifold for solid-phase extraction (SPE). SPE cartridges, shown on top of manifold, are available from Waters Corp.

17. Sample Composites

Because of the small surface area of the POCIS, which is related to the amount of chemical sampled, it is a common practice to composite the extracts of two or more POCIS into a single extract in order to increase the amount of chemical present in the extract for detection. This practice aids in the detection of compounds expected at very low concentrations in the environment and when the sampling rate for a target chemical is very low or short exposure times were used resulting in minimal volumes of water extracted. Typically, individual POCIS are extracted as described above and the extracts are combined at the evaporation step. The three

POCIS that are housed in the commercially available small POCIS canister have been generally successful for monitoring of MC at UWMM sites thus far (Rosen et al. 2016, 2017).

18. Estimating Water Concentrations from POCIS Data

The analytical laboratory will provide the user chemical concentration data in a raw form that will require additional data processing in order to quantify water concentrations. The data will usually be reported as nanograms of a chemical per sampler, where the sample will be the passive sampler extract. If the data are reported as an extract concentration, ng/sampler can be calculated by multiplying by the volume of the extract.

Estimating water concentrations from POCIS data is contingent on the availability of experimentally-derived R_s data. Based on the R_s values presented in **Tables 2 and 4** for multiple MC, concentrations can be expressed on a ng/L TWA basis.

Assuming that the chemicals of interest sampled by the POCIS remain in the integrative phase of sampling for the deployment time, the use of the integrative uptake model for the calculation of ambient water concentration is justified (see Equation 1 above).

In cases where R_s data for a specific chemical are not available, the result should be reported as mass of chemical sampled per POCIS (ng/POCIS), resulting in a more qualitative estimate of the TWA, but can be used to indicate the presence or absence of a chemical. With regard to the detection limit, this information can be useful in determining the relative amounts of a chemical present at each site (ranking of sites).

19. Data Analysis and QA/QC

Coordination with analytical lab and holding times

The study needs should be discussed with the analytical laboratory before beginning fieldwork. Many analytical laboratories have not worked with POCIS and may be uncertain of how to process the media or extract chemicals from it. POCIS extracts are generally easier to work with than samples of other environmental matrices and should be analyzed by standard instrumental techniques the lab uses for other matrices, such as water or sediment extracts. The sorbent used in the POCIS is also commonly used in SPE applications, and therefore, should be readily processed in the same way that most labs process SPE used for extraction of contaminants from water samples. The commercial vendor of the POCIS offers sample extraction as a service. See **Section 16** for a description of extraction procedures.

The reporting procedures of a laboratory should be discussed as many laboratories use automated reporting systems set up to report in the units of ng/L of water. These units are not suitable for a passive sampler extract as the desired units should be reported as total ng of chemical per POCIS or combined replicate POCIS, as in some cases, POCIS deployed at the same site may be pooled into a single extract to increase sensitivity or decrease variability. The unit of ng/POCIS is required for the calculations to estimate ambient water concentrations. These instructions will need to be communicated to the laboratory.

Once frozen, POCIS have a longer holding time than water samples. They should be held up to 72 h at 4°C while transferred to the environmental laboratory. Once at an analytical laboratory, they can be frozen for up to 28 d prior to extraction and analysis.

Quality Control

Quality control for POCIS will have the same general procedures as for other types of samples. For each sampling trip, a blank passive sampler (field blank) should be subjected to all phases of the field and transport experience. During the deployment and retrieval operations (the time the field passive samplers are exposed to air), the lids to the field blank containers are opened allowing exposure to the surrounding air. Field blanks account for contamination during transport to and from study sites, exposure to airborne contaminants during the deployment and retrieval periods, and from storage, processing and analysis. These samples should be extracted and analyzed along with field samples in an effort to check for contamination.

Extraction and procedural efficiency should be measured using surrogates in each sample. Preferentially, stable isotopes of munitions constituents should be used, or other related compounds suggested by the analytical method (EPA 8330 or 8095). As with all standard methods, procedural blanks, spikes and spike duplicates should be conducted at a frequency of at least 5% of samples extracted. Spiking analytes into the sorbent to conduct laboratory spikes can be challenging due to dispersal. Spiking using a solvent carrier can be conducted directly to sorbent followed by careful mixing. Alternatively, a water carrier can be used to load the munitions constituents on the sorbent after the sorbent is loaded into an SPE cartridge (similar to a standard SPE extraction).

Quality control for instrumentations will be based on the chosen analytical technique and will not be different than required for other matrices.

Data management and analysis

Data management and analysis will be conducted similarly as per all other matrices. The exception as noted is that concentrations should be reported as mass of analyte/POCIS. From these units, water concentrations can be calculated using the standard equations for converting mass accumulated to a TWA concentration, provided in **Sections 3**, with the inclusion of flow rate-specific sampling rates, if available, as shown in **Section 14**.

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14. ABSTRACT

The 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 and unexploded ordnance, as a result of historic military activities. In addition to explosive blast (safety) considerations, regulators are increasingly concerned about potential ecological impacts of MC on the marine environment. Although UWMM have the potential to corrode, breach, and leak munitions constituents (MCs) such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-s-triazine (RDX) into aquatic environments, several challenges prevent accurate assessment of environmental exposure, based on the uncertainties associated with munition presence, condition, propensity for leakage, rapid transformation of some MC, and likelihood for highly localized exposure.

This demonstration focused on field validation of commercially available passive sampling devices, specifically Polar Organic Chemical Integrative Samplers (POCIS), for estimating time averaged water concentrations at underwater sites. Previously calibrated for detection of MC in laboratory-based studies, this report provides new results from further optimization efforts, and provides results from two field studies, including a positive control field study in Santa Rosa Sound, Florida, and a larger scale effort conducted in a bay adjacent to the former Vieques Naval Training Range at Vieques Island, Puerto Rico.

15. SUBJECT TERMS

munitions; POCIS; TNT; RDX; time-weighted average; passive sampling; laboratory calibration; flume; TNT; RDX

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