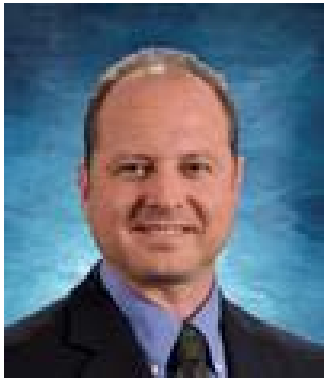
Validation of Passive Sampling Devices for Monitoring of Munitions Constituents in Underwater Environments



Gunther Rosen
SPAWAR Systems Center (SSC) Pacific

SERDP DOD • EPA • DOE | ESTCP

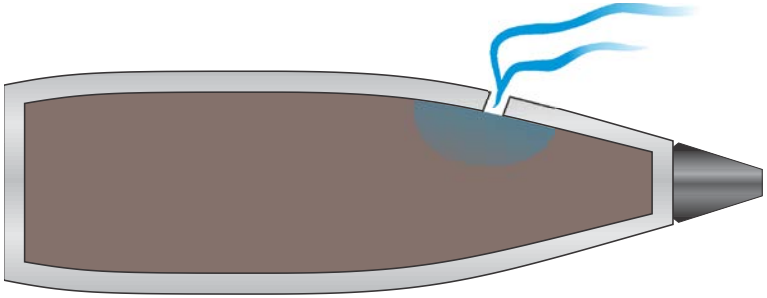
Agenda

- Problem statement
- Technology overview
- Calibration for munitions constituents (MC)
- Positive control field study results
- Refinement of sampling rates for flow velocity
- Validation at former Vieques Naval Training Range
- Technology transition

Problem Statement

- Increasing regulatory scrutiny to assess MC exposure and potential for associated ecological or human health effects
- Multiple factors may prevent accurate assessment

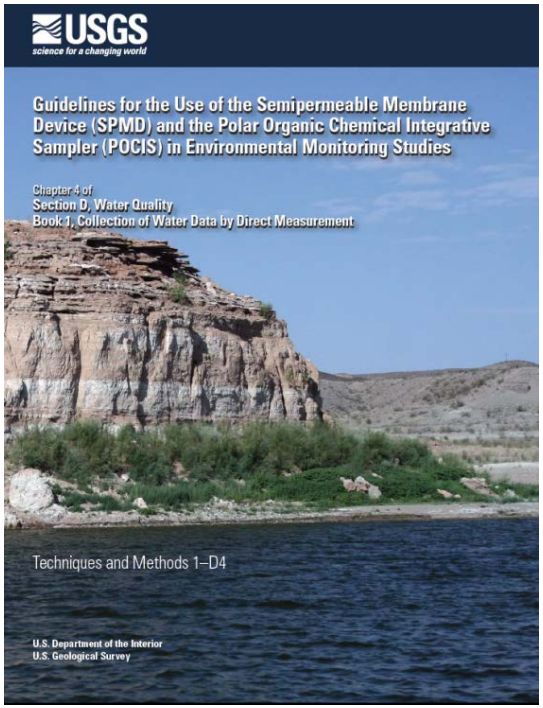
Dissolution	Hole size	Corrosion
Currents	Biofouling	Cavity radius
Tides	Water chemistry	Saturation



POCIS Technology

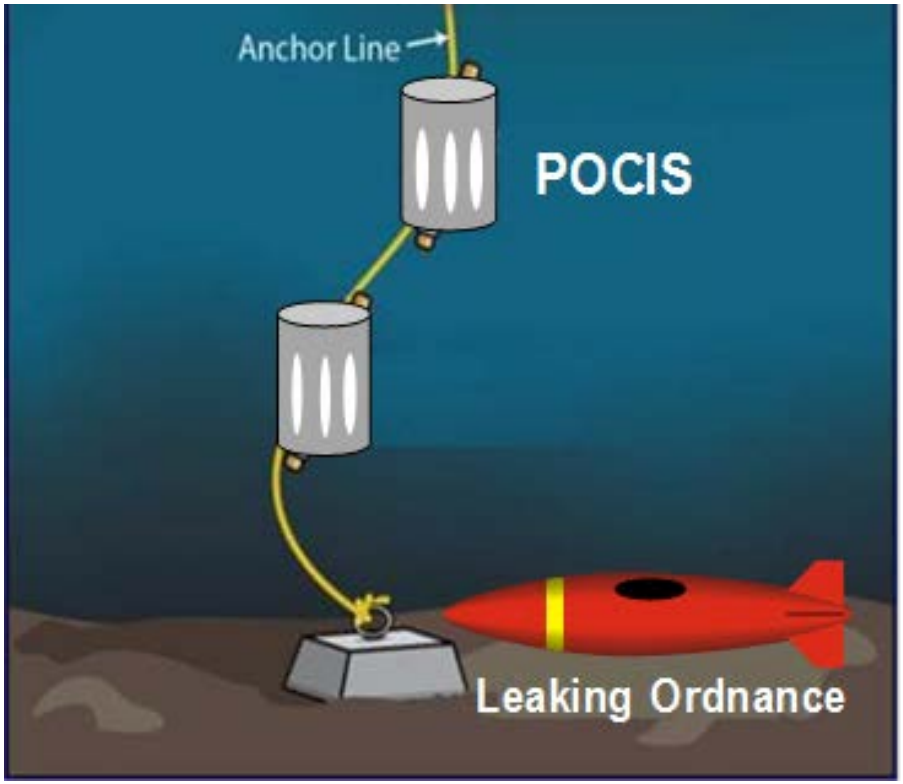
Continuous, Integrative Sampling

- Weakly hydrophobic organics (Log Kow <1-3)
- Oasis HLB sorbent encased by polyethersulfone membranes
- Long time to equilibrium
- Standard methods*



*Alvarez et al., 2010. http://pubs.usgs.gov/tm/tm1d4/

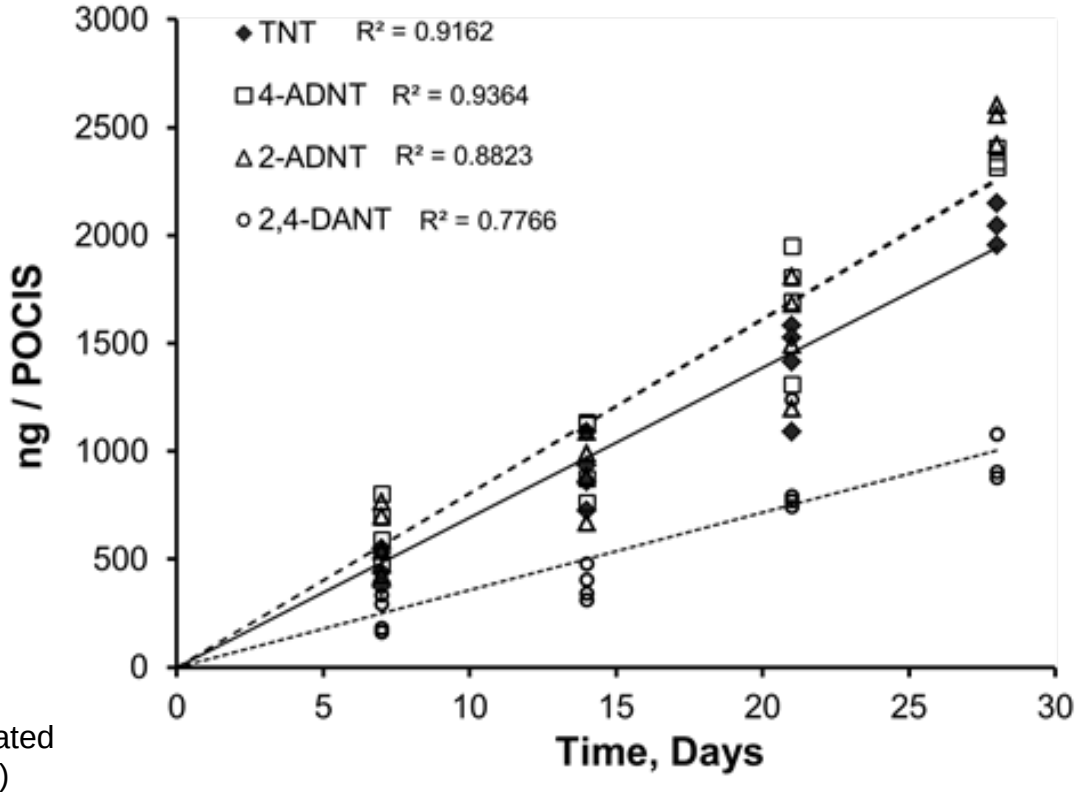
POCIS Sampling for UXO



Calibration for MC

*Derivation of Sampling Rates (Rs)**

- TNT
- 2-ADNT
- 4-ADNT
- 2,4-DNT
- 2,6-DNT
- TNB
- DNB
- 3,5-DNANIL



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

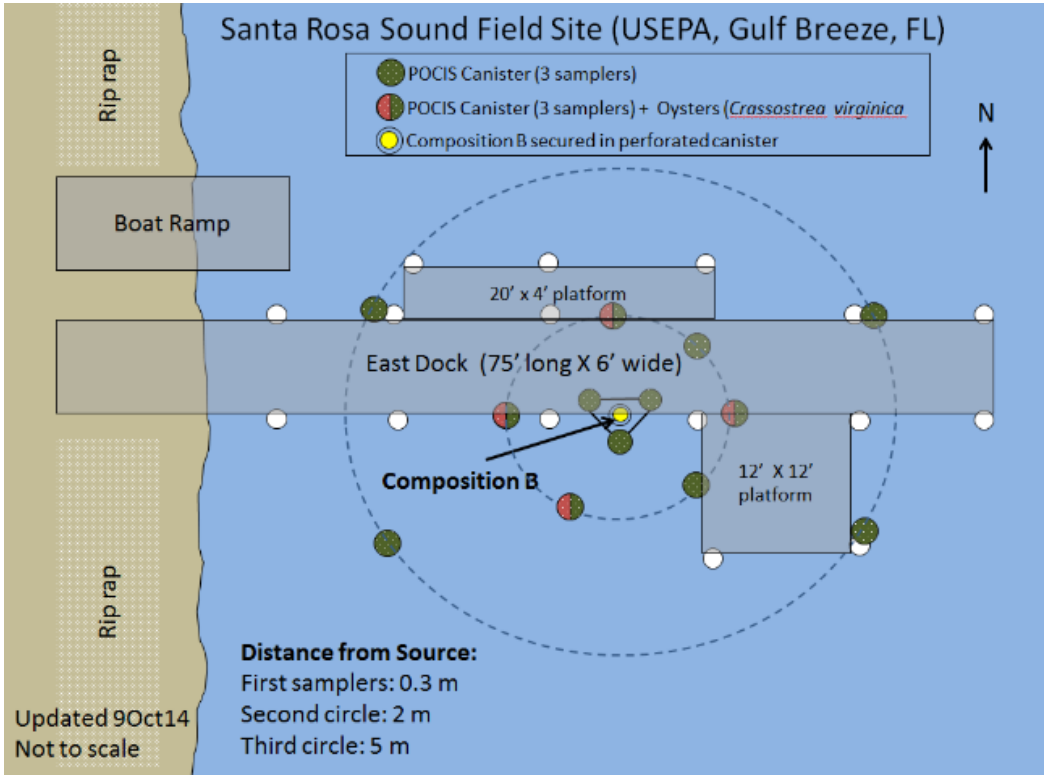
C_w = TWA Concentration
N = mass chemical accumulated by sampler (typically ng)
R_s = sampling rate (L/d), and
T = exposure time (d)

*Belden et al. 2015. Environ. Toxicol. Chem. 34:959-967, and this project

Controlled Field Validation

EPA Gulf Ecology Division, Santa Rosa Sound, FL

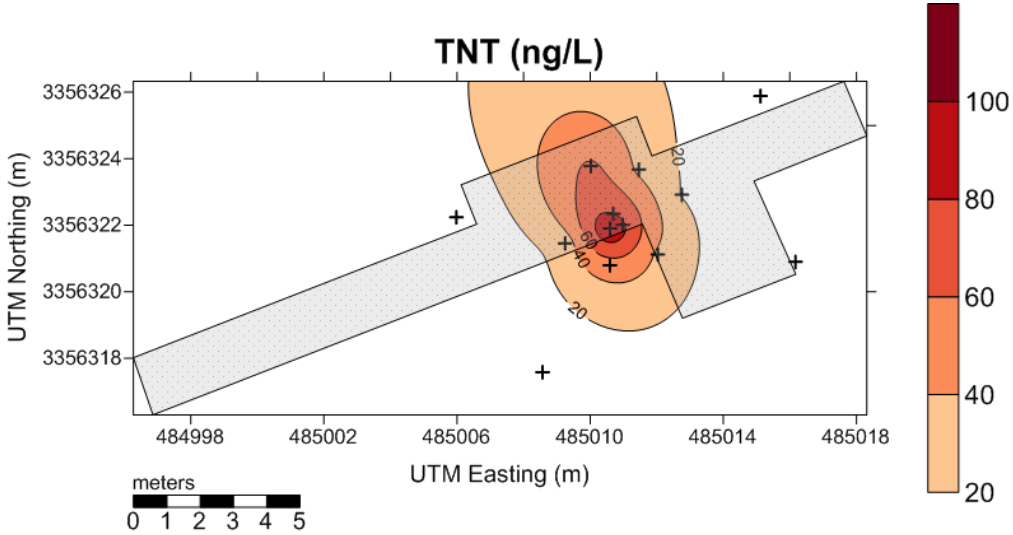
- Point source: 15 g Composition B (100 - 200 mg fragments)
- 2-week exposure

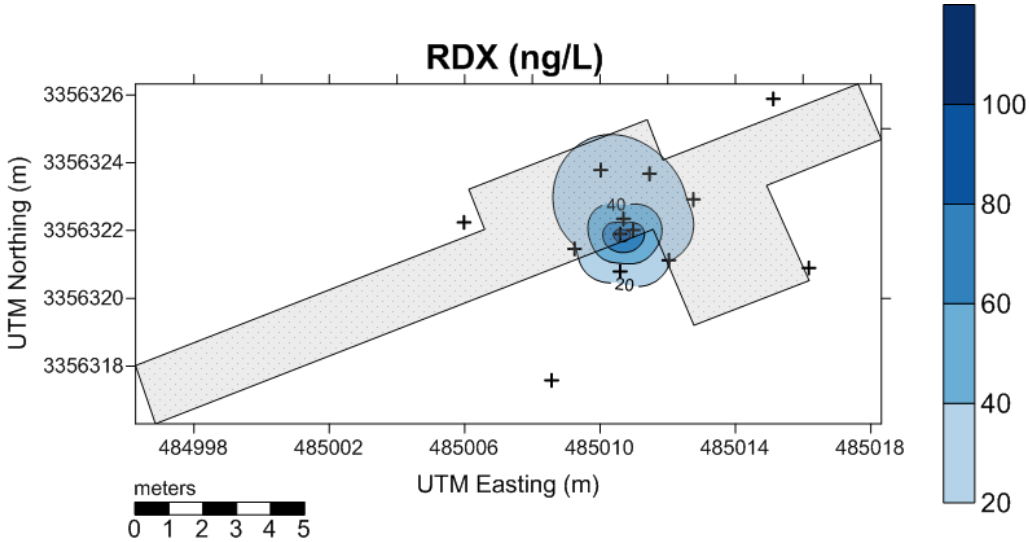


Authorizations: EPA Gulf Ecology Division; Florida Department of Environmental Protection; USACE Nationwide Permit #5

Controlled Field Validation

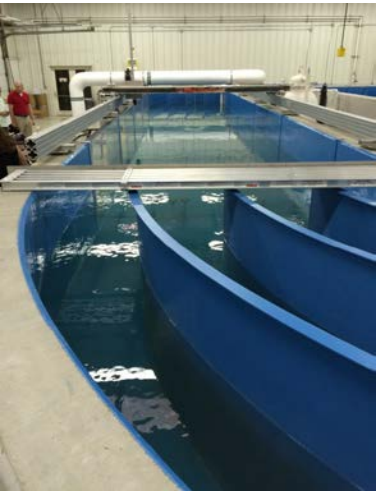
- Gradient away from source canister
  - Detectable 2 m from source
  - Non-detectable 5 m from source
- 9 - 103 ng/L, where detected
- Detection limits ~6 ng/L
- Reporting ~18 ng/L
- Grab water (1L) and tissue samples below detection limits

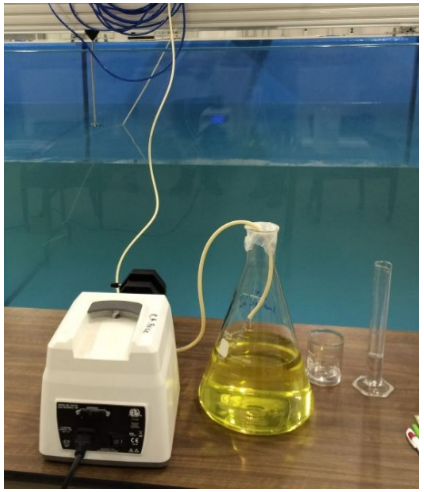


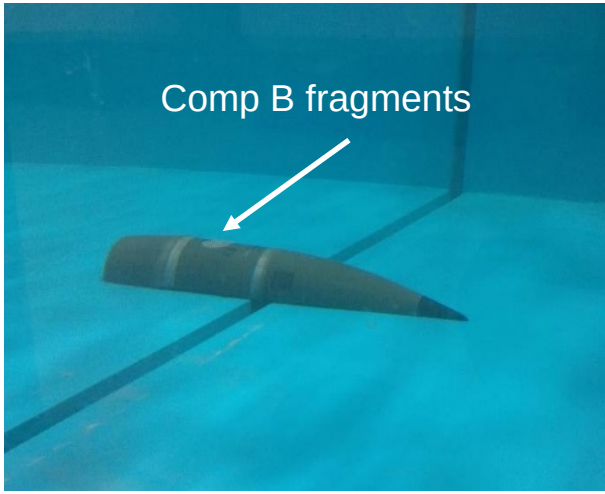


Calibration to Optimize POCIS Sampling Rates (Rs)

- Flow rate primary factor affecting POCIS sampling rates [1,2]
- 30,000 gallon two-sided flume
- Spiked flume with a MC “cocktail” at 1 µg/L
  - Multiple 10-day experiments with different flow rates
- Composition B explosive fill: open vs encapsulated fragments
- Calibration with daily grab sampling



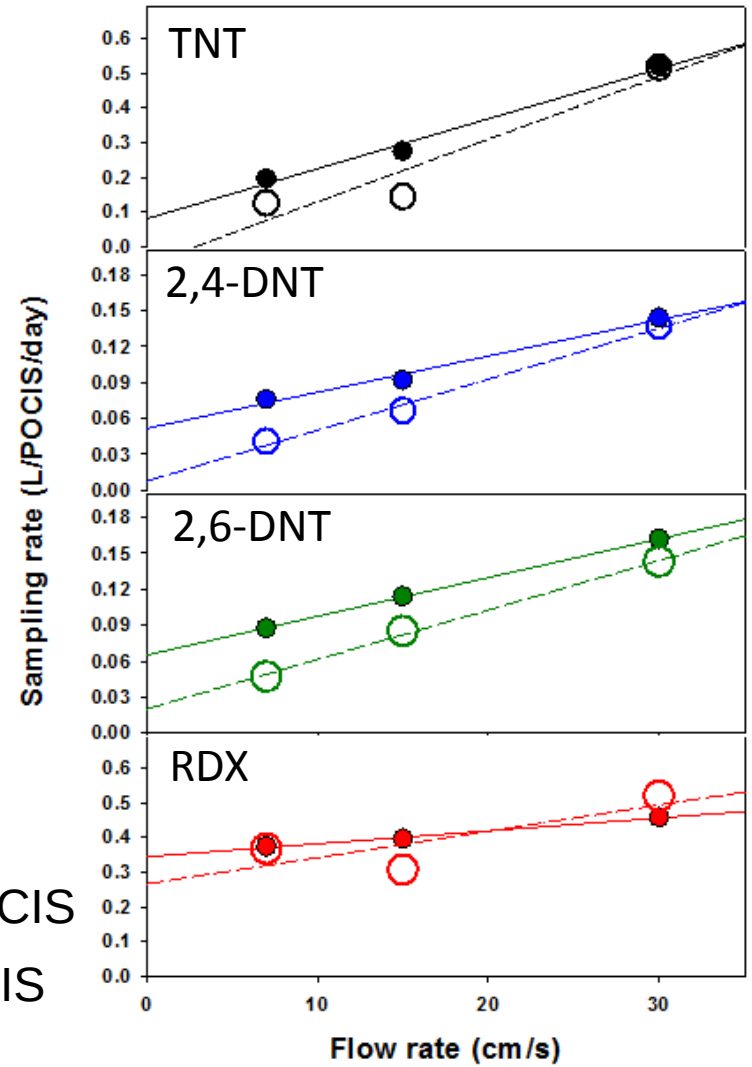




[1] Harman et al. 2012. Environ. Toxicol. Chem. 31: 2724-2738
[2] Morin et al. 2012. Trends in Analytical Chemistry 36:144-175

Sampling Rates (Rs) for Multiple Flow Velocities

- TNT, DNTs have flow dependence, sampling rate differs by factor of ~2
- RDX sampling rate less affected, differs by factor of ~1.5
- Equations more accurately estimate MC water concentration when site-specific flow rates are measured during deployment
- Example for TNT (uncaged)
  - Rs= 0.081(flow rate) + 0.014

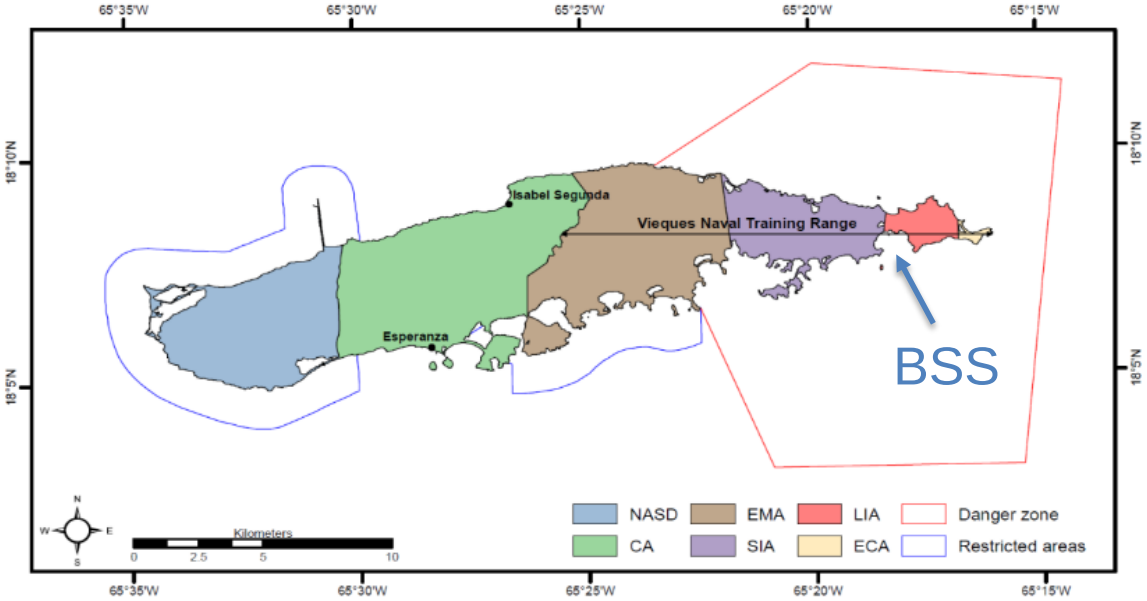


● Exposed POCIS

○ 'Caged' POCIS

Field Validation at Vieques, PR

- Live Impact Area (LIA) at former Vieques Naval Training Range
- Air-to-ground bombing, gunfire from 1941 - 2003
  - Site: Bahia Salina del Sur
  - Collaboration and coordination with NAVFAC site managers, CH2M Munitions Response and Scientific Divers, and local stakeholders

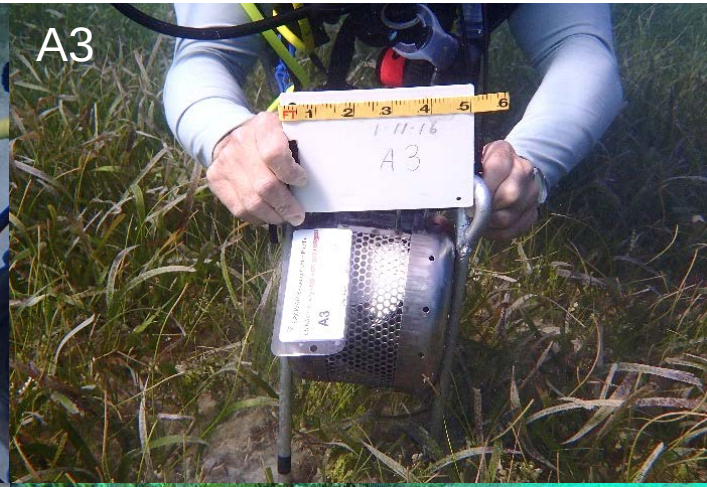


Former training at Bahia Salina del Sur

Bauer and Kendall, 2010. NOAA

Field Validation at Vieques, PR

- Selection based on Reconnaissance survey 1 month prior to deployment
- Critically assessed by MR divers for likelihood to contain MC
- Represented range of conditions, type (MK series bombs vs projectiles), location

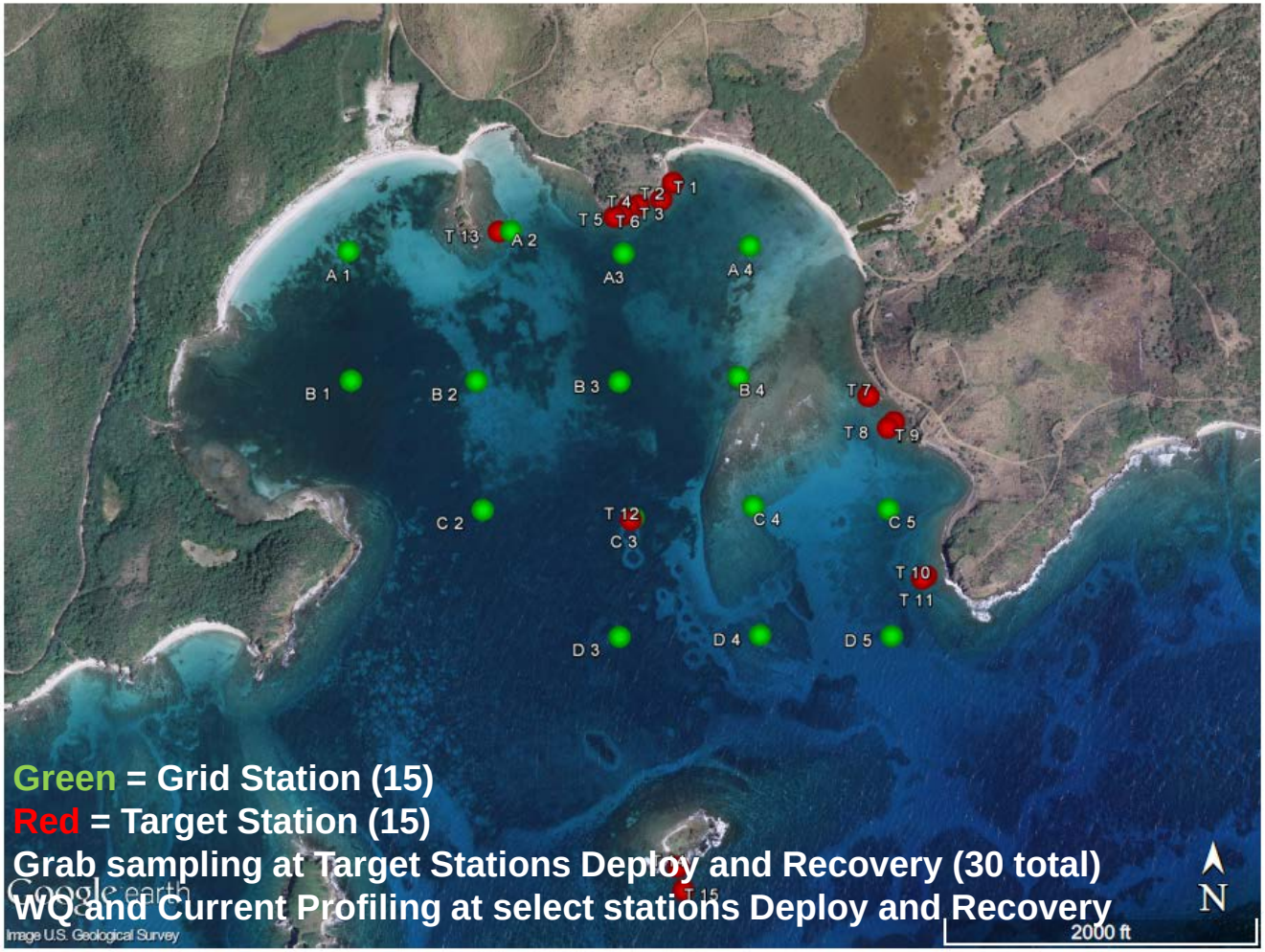


Test Design

- 15 Target station samplers (6 - 12” from items)
- 15 Grid stations
- Grab water samples on deploy and recovery
  - 1 L collected collocated with POCIS 6 - 12” from Targets
  - All water and POCIS analysis was by EPA 8095 modified for GC/MS with negative chemical ionization (Belden et al., 2015)
  - EPA 8330 can be used as well

Sampling Locations, Bahia Salina del Sur

January 2016

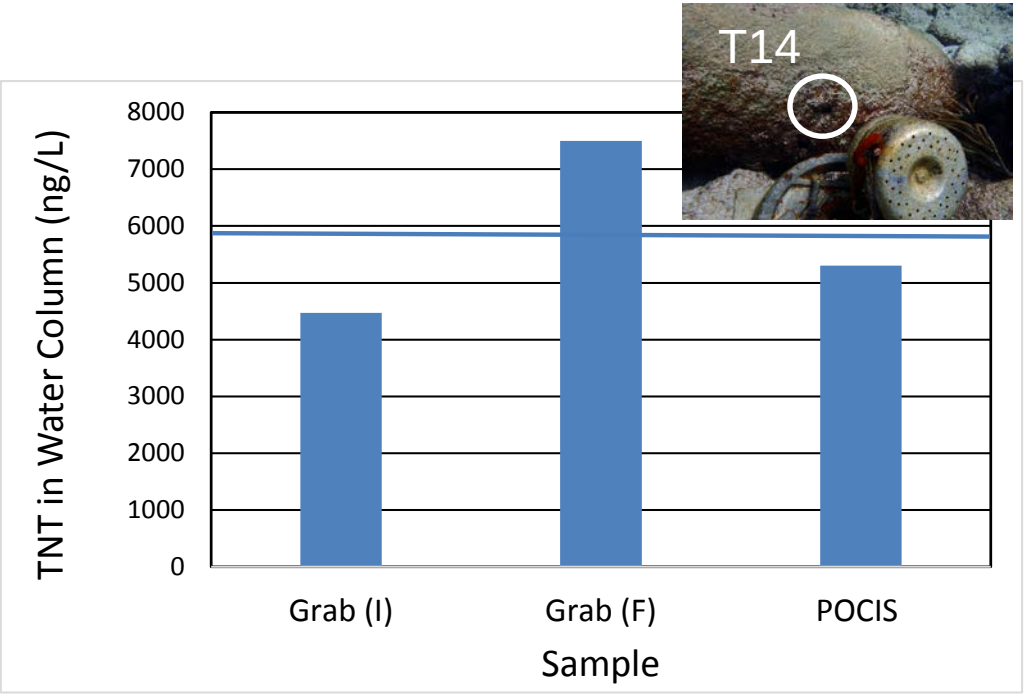


Aerial image © 2016 Google Earth.
Annotation © 2016 SPAWAR Systems Center Pacific

Video

Results at Bahia Salina del Sur

- 100% of samplers recovered intact
- TNT and degradation products
  - 1 of 15 targets above Reporting Limit
    - 1,000 lb General Purpose Bomb
    - Visible breaches
    - TNT at low **µg/L** concentrations
    - TWA concentrations similar to grabs
- RDX
  - POCIS-measured RDX at ultra-trace (**low ng/L**) levels for 79% of Target stations
  - For grab water, RDX detected in only 21% of stations

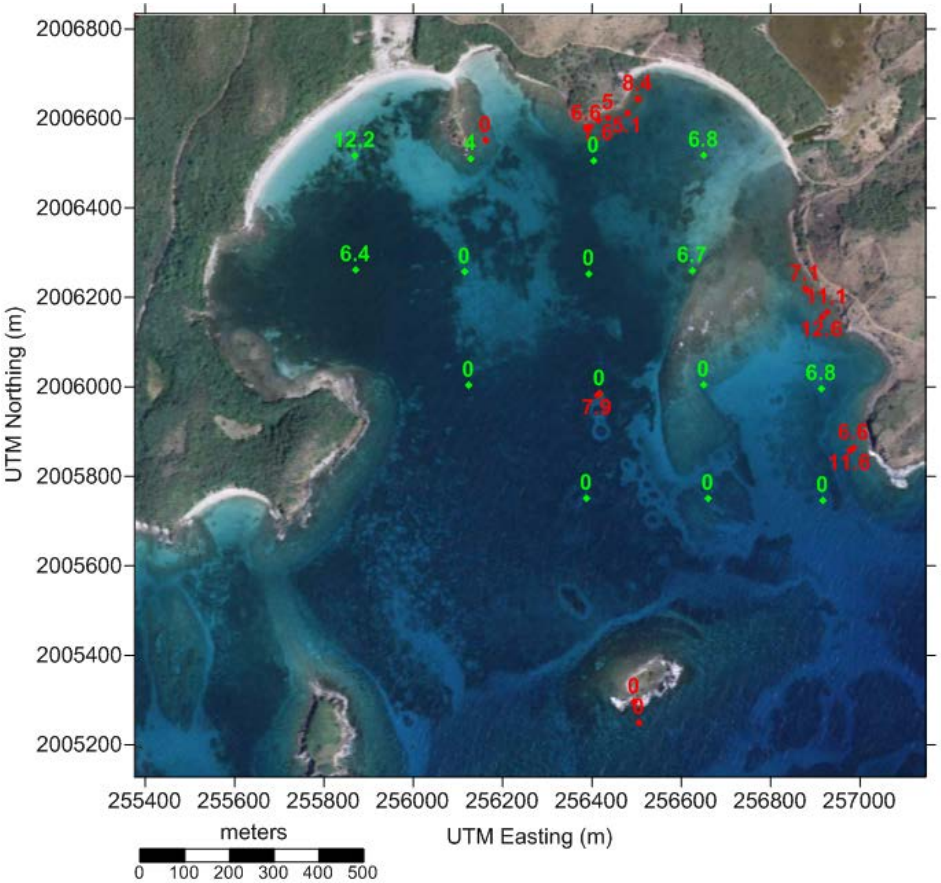


Sample Type	Constituent	# samples	# detects	Detect frequency (%)	Concentration range (ng/L)	MDL (ng/L)	QL (ng/L)
POCIS	TNT	14	1	7	5304	3.7	11.1
	RDX	14	11	79	5.0-12.6	2.9	8.8
Grab - Initial	TNT	15	1	7	4470	8.4	25
	RDX	15	3	20	24-51	18	54
Grab - Final	TNT	15	1	7	7497	8.4	25
	RDX	15	0	0	0	18	54

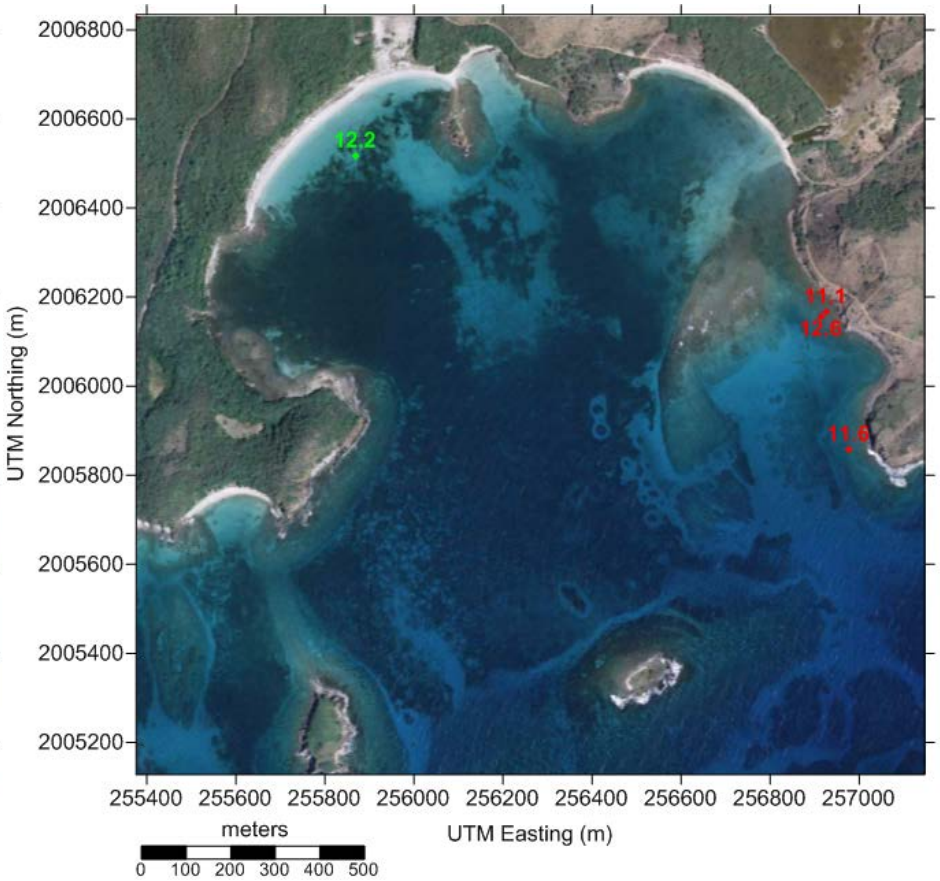
POCIS-Derived RDX Results

Detects concentrated around bay perimeter

17 of 29 (59%) samples above MDL

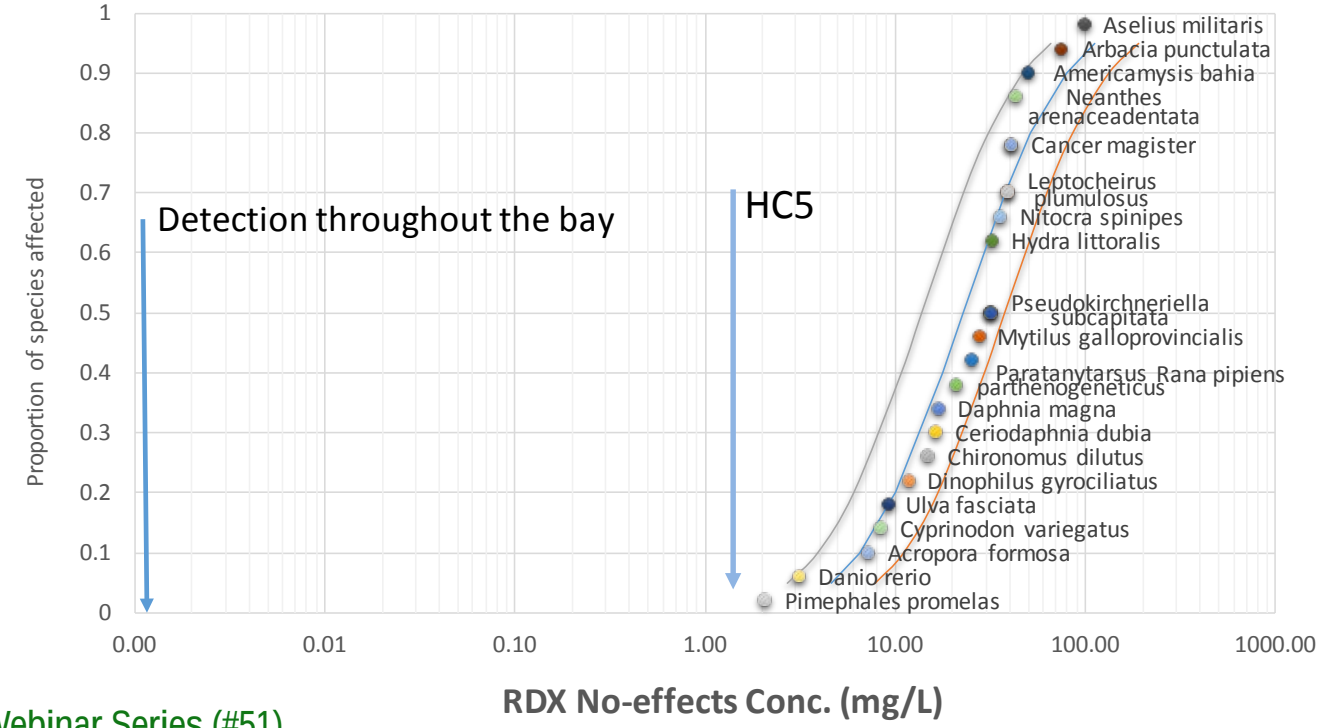


4 of 29 (14%) samples above RL



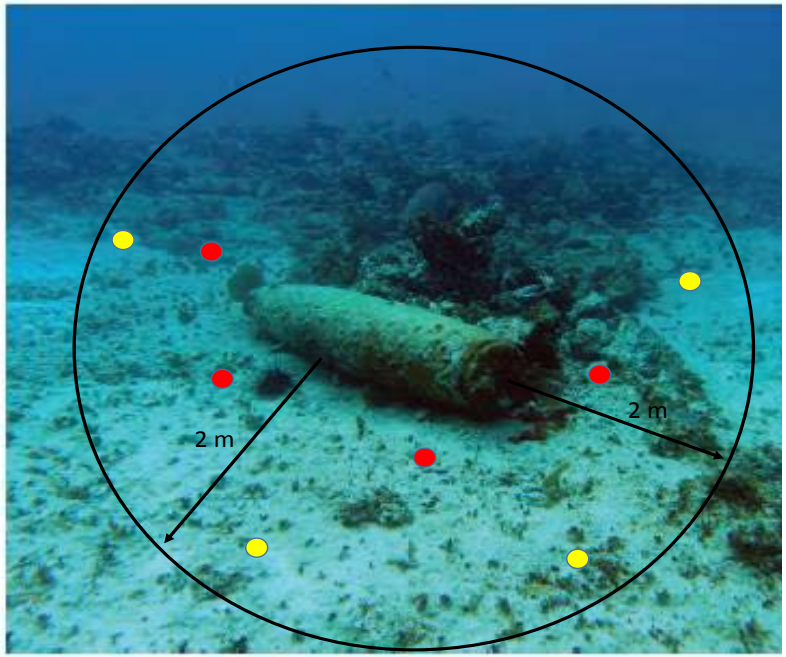
Ecological Relevance

- Highest TNT detects 2 orders of magnitude lower than Hazardous Concentration (to the 5% most sensitive species)
- RDX detects 6 orders of magnitude lower



Sediment Sampling, Bahia Salina del Sur

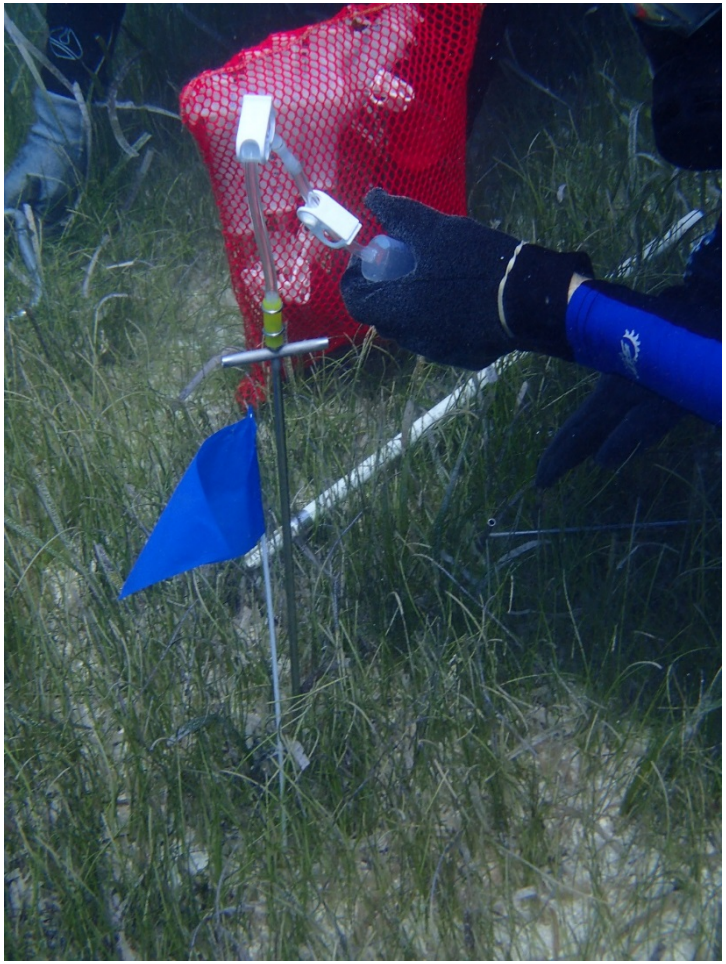
- 4 stations (A1, T10, T11, T12) where RDX was detected by POCIS
- Pore water collected with PushPoint samplers ~0.5 and 2 m around items, 4 pushes around item
- Sediment collected with 6” tall core liners for MC, TOC, grain size



Sediment Sampling Results

All sediment and pore water analytes below MDLs

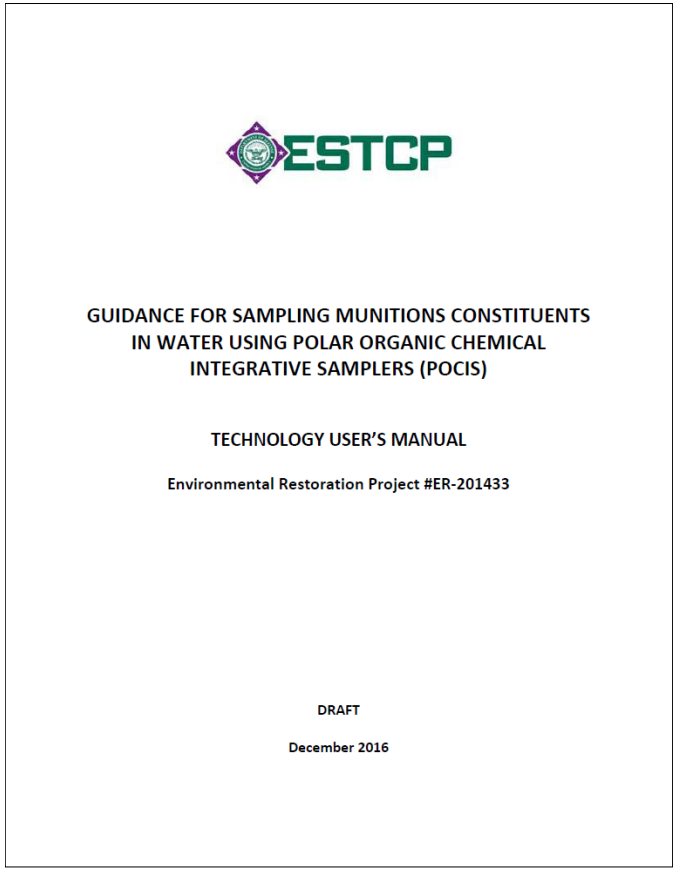
	Pore water (ng/L)		Sediment (ug/kg), dw	
Analyte	**MDL**	**QL**	**MDL**	**QL**
TNB	3	9	0.6	1.8
TNT	8	25	1.6	4.8
2,6DNT	3	8	0.5	1.5
2,4DNT	9	28	1.8	5.4
DNB	6	17	1.1	3.3
RDX	18	54	3.4	10.2
4ADNT	8	25	1.6	4.8
2ADNT	6	17	1.1	3.3
3,5DNANIL	12	36	2.3	6.9



MDL=method detection limit
QL= quantitation limit

Technology Transition

- End user guidance document (in preparation)
- Samplers are already commercially available
- Interactive site demonstration at Vieques (site managers, MR divers, regulators, stakeholders)
- EPA visibility through controlled field study at Gulf Breeze, Florida
- Multiple webinars provided to DoD community
- Multiple peer-reviewed publications (2 published, 3 in preparation)


ESTCP

GUIDANCE FOR SAMPLING MUNITIONS CONSTITUENTS IN WATER USING POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS (POCIS)

TECHNOLOGY USER'S MANUAL

Environmental Restoration Project #ER-201433

DRAFT

December 2016

Conclusions

- POCIS successfully validated for assessing MC exposure at Underwater Military Munitions sites
  - High sensitivity (low detection limits)
  - Useful for potential time-varying conditions (e.g., leakage, tides)
- Positive control and Vieques site results validate laboratory studies suggesting highly localized/negligible exposure and low potential for ecological risk
- Benefit to DoD is accurate assessments resulting in appropriate management decisions (e.g., leave in place versus removal)
  - Potentially reduces public or regulatory perception that sampling is being conducted at the wrong time and place, and with insufficient detection capabilities
- Costs analysis and DoD User's Guide in process, available Spring 2017

Acknowledgements

- Co-funding provided by the Navy's Environmental Sustainability Development to Integration (NESDI) Project #465
- Dr. Robert George, Bill Wild, Molly Colvin, Joel Guerrero (SSC Pacific)
- Dr. Jason Belden, Dr. Shane Morrison, Krystal Sieve (OSU)
- Dr. Gui Lotufo, Dr. Christa Woodley, Dr. Dave Smith, Lauren Rabalais, Jim Biedenbach (USACE ERDC)
- Dr. Stephen Fallis and Gregory Ostrom (Naval Air Warfare Center Weapons Division, China Lake)
- Dr. Mace Barron and Jason Mangum (USEPA Gulf Ecology Division)
- Dan Waddill, Kevin Cloe, Dan Hood, Madeline Rivera (Vieques Site Restoration Managers from NAVFAC LANT)
- CH2M Munitions Response and Scientific Dive Teams
- Diane Wehner (NOAA)
- Nick Hayman and Jacob Munson (SDSU Research Foundation)

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-201433

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