FINAL REPORT

Development of an In Situ Passive Sampler for the Detection and Remediation of Explosive Compounds

SERDP Project ER-2539

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University of Connecticut

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14. ABSTRACT

The abundance of aging unexploded ordnances (UXOs) in marine continental margins and nearshore areas is a global scale concern. Though it is impractical to retrieve these UXOs in their entirety it is critical to establish cost effective methods with which areas at risk may be monitored or evaluated for leakage and to measure concentrations of energetic compounds derived from UXOs to compare with water quality criteria. In this effort a novel passive sampling approach based on the introduction of samplers coated with ethylene vinyl acetate (EVA) were evaluated to assess the efficacy of these samplers to fulfill the gap in marine water and porewater monitoring. These initial efforts were dedicated to parameterizations identifying the uptake and depuration rates to confirm sufficient deployment times.

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List of Acronyms

CHEMSEA – Chemical Munitions Search and Assessment http://www.chemsea.eu/
DNX – 2,6 or 2,4-dinitrotoluene
ER2539 – project identifier
EVA – ethylene vinyl acetate
NG - nitroglycerine
OTT – octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
PETN – pentaerythrotol tetra nitrate
RDX – 1,3,5-trinito-1,3,5-triazine
SEED – SERDP Exploratory Development
SERDP – Strategic Environmental Research Development Program
Tetryl – 2,4,6 trinitrophenylmethylnitramine
TNT – 2,4,6-trinitrotoluene
UXOs – unexploded ordnances

Keywords

Acknowledgements

I.   Abstract

The abundance of aging unexploded ordnances (UXOs) in marine continental margins and nearshore areas is a global scale concern. Though it is impractical to retrieve these UXOs in their entirety it is critical to establish cost effective methods with which areas at risk may be monitored or evaluated for leakage and to measure concentrations of energetic compounds derived from UXOs to compare with water quality criteria. In this effort a novel passive sampling approach based on the introduction of samplers coated with ethylene vinyl acetate (EVA) were evaluated to assess the efficacy of these samplers to fulfill the gap in marine water and porewater monitoring. These initial efforts were dedicated to parameterizations identifying the uptake and depuration rates to confirm sufficient deployment times. The samplers exposed to contaminated waters underwent a rapid uptake within two hours of deployment in the kinetic uptake phase and reached steady state/equilibrium within 6 hours. TNT kinetics were slightly faster than those of RDX. It was discovered that by altering the percent acetate of the EVA film the uptake of RDX could be enhanced significantly above expected predictions based on octanol water partitioning. This was attributed to the influence of the polar acetate group and likely due to dipole-dipole interactions between acetate and nitrate goups. This enhancement was also true for TNT though to a lesser degree. Compound integrity within the film was stable once refrigerated for up to three months and this can be extended if samples are frozen. Both effects of salinity and temperature were evaluated in order to improve targeted designs and back calculations of aquatic concentrations. $LogK_{EVA-w}$ varied inversely with temperature at -0.01units per ^oC increase. Salinity has not significant effect on equilibrium values. The extraction process was improved to two hours per sample from the time of arrival to the lab to the time of analysis. This could likely be further reduced with faster solvent reduction techniques.

The ultimate test of the sampler involved sampling at sites of known UXO dumping where energetic compounds have been detected. Deployment in Halifax Harbor detected three of the target compounds in our laboratory analysis followed by confirmation and identification of several more energetic compounds confirmed by ALS labs. ALS detected significant concentrations of our target compounds in addition to pentaerythrotol tetra nitrate (PETN), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (OTT), nitroglycerine (NG), 2,4,6 trinitrophenylmethylnitramine (Tetryl). These compounds are in the ppb ranges and were not detected in earlier studies.

The second deployment in the Baltic Sea at a known munitions dumping site, Gdansk Deep, also yielded significant concentrations of TNT, RDX and two di-nitro TNT derivatives from our laboratory. Confirmation from ALS labs also identified presence of Tetryl, NG, OTT and PETN in these samples. These results provide excellent confirmation of the utility of these non-specific samples wherein 2 to 5 g of film are sufficient to capture trace environmental concentrations of energetic compounds and their derivatives.

Our field test of the samplers have shown promising results worthy of further investigation. It is our intention to further analyze duplicate samples from field sites in collaboration of Dr Paula Vanninen from the University of Helsinki who is a global leader in munitions compounds in order to further identify compounds of interest (particularly key toxic breakdown products) that

these non-specific samplers may have captured. We are also very interested in deploying the samplers at additional sites where climate and bottom sediments may vary. An additional future goal is to evaluate the possibility of direct uptake of the EVA polymer from a leaking UXO, minimizing contamination of the surrounding ecosystem. Other follow up efforts include:

- How are does the sampler perform in a range of sediments and redox conditions?
- How do natural ranges of dissolved organic matter influence the sampler?
- What is an appropriate spatial and temporal resolution for mapping of TNT, RDX and their derivatives in the field?
- Can the sampler be segmented to provide sediment depth profiles and at what resolution?
- Can an EVA coated mesh be used in sediment systems for remediation?
- Does impregnating the EVA with a carbon resin shift the sorption and remediation properties?
- Further optimization of the methodologies and development of standard operating procedures
- How do the optical properties of the EVA film change when it has sorbed the target compounds? (this is to assess potential for real time monitoring)

II.   Objectives

This project set out to conduct the necessary calibration and sensitivity tests of a passive thin-film equilibrium sampler using ethylene vinyl acetate (EVA) for optimization and deployment in sediments of active and legacy artillery ranges to detect and remediate target munitions compounds 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and their derivatives).

Specifically:

Objective 1: Evaluate EVA sampler uptake and offloading rates for the target munitions compounds as a function of ambient concentration and film thickness.

Objective 2: Assess the stability of target compounds within the sampler film for deployment timescales.

Objective 3: Optimize sampler geometries and film thicknesses for the detection of target field concentrations (below nanograms per liter).

Objective 4: Deploy sampler onsite to demonstrate mapping field distributions of target compounds and identifying accumulation zones.

BENEFIT: The EVA sampling approach provides *in situ* spatial and temporal sampling at biologically relevant concentrations of contaminants. The sampler shows promise for a broad range of hydrophobic contaminants including TNT and RDX which are the focus the ER 2539 project. The potential as a remediation technique may lead to minimizing exposure risk and avoiding costly dredging approaches.

- A reliable and simple quantitative passive sampler for *in situ* sampling of munitions compounds over a wide range of solubilities
- Environmentally safe/preferable sampler (non-toxic material)
- Cost-effective
- Versatility in freshwater, saltwater and porewaters environments
- Multiple depth deployments (no pressure issues)
- Synoptic spatial and temporal mapping
- Highly sorbent "fly-paper like" affinity for organic munitions compounds may lead to targeted and safe in situ remediation without risk to humans and marine life

III.   Background

Over the last century the number of unexploded ordnances (UXOs) that have accumulated in coastal waters has led to concerns with regards to unintentional risks associated with trolling, bycatch and inevitable leakage from aging and corroding shells. Though there are clear reasons why the removal of these UXOs may be impractical, screening and assessing the risks associated with them is needed to provide avoidable harm. Cost effective methods are in need to monitor sediment and aquatic concentrations of munitions compounds and their often more toxic breakdown products (Nippera et al., 2005) in order to gauge risk according to sediment quality criteria (Pascoea et al., 2010) and classify both areas containing UXOs and active artillery training sites.

One of the greatest limitations in the evaluation of dissolved explosive concentrations and the associated impacts is the limited resolution of data and the cost prohibitive nature of continuous sampling. Added to this is the lack *of in situ* detectors that prevents any synoptic spatial assessment of contaminant plumes which would be of great value. Short of multiple mass spectrometers in the field (Syage et al., 2001) there is no real-time option for organic contaminant measurements. One way of overcoming this limitation is the use of passive chemical samplers that may be deployed at multiple sites simultaneously to compose a spatially resolved distribution of a given compound. Passive samplers have been designed as biosamplers since the 1980's (Huckins, 1989, Huckins et al., 1990) and have only recently been applied to global and regional atmospheric sampling (Genualdi et al., 2010). Aquatic and sediment sampling with passive samplers is now considered a feasible sampling approach and several types of passive sampling devices have been proposed (Alvarez et al, 2004, Allan et al, 2010, St. George et al., 2010). Depending on the nature of the target compounds, passive samplers may be designed such that the affinity of the sorbing phase may be optimized (ie very non-polar or polar) though a broad spectrum sampler can have the advantage of detecting more organic compounds including their organic breakdown products. This study utilizes an ethylene vinyl acetate (EVA) polymer as the sorbent phase of choice.

EVA has an acetate group on each monomer that gives the polymer a hydrophobic and hydrophilic moiety (Figure 1). This amphiphilic nature enables it to have a "fly paper-like" affinity for a wide range of organic compounds over a wide range of solubilities.

Figure 1: Structure of ethylene-vinyl acetate thin-film (EVA)
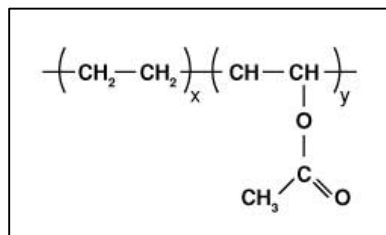
Its affinity for organic compounds mirrors that of octanol which makes the octanol-water partition coefficient (K_{ow}) a useful proxy for EVA deployed in aquatic environments. To date the sampler has been calibrated over Log K_{ow}'s of 1.5 to 10 using TNT, RDX, halogenated

pesticides and polybrominated flame retardants (St. George et al., 2010). The equilibrium partition coefficient for EVA and water (K_{EVW-W}) has be estimated reliably using K_{OW} and the results in both salt and freshwaters result in the empirical correlation of Equation 1 (St. George et al., 2010) where

$$\text{Log } K_{EVA-W} = 1.04 \text{ Log } K_{OW} + 0.22 \tag{1}$$

The expression shows that EVA has an affinity for organic compounds in water that is slightly greater than that of octanol over a broad range of target solubilities. For munitions this translates into highly sorptive material that can effectively partition and potentially remove compounds from the exposed environment.

Detection limits: The detection limits of the EVA sampler can be tuned to the environmental concentrations based on the amount of EVA applied and an adjustment of the surface area to maintain a thin film. Equation (1) provides the critical parameter for field applications such that K_{EVA-W} can be derived using a known or estimated K_{OW}. The required mass of EVA (M_{EVA}) can be determined using the expected field concentration ranges (C_W) and the analytical detection limits in grams or moles per unit volume (N_{target}).

$$M_{EVA} = N_{target} \, \rho_{EVA} \, (K_{EVA\_W} \, C_W)^{-1} \tag{2}$$

where ρ_{EVA} is the density of EVA (0.93 g cm^{-3}). Thus detection limits for organic compounds in the field can be readily achieved in the ppb range. This enables simultaneous sampling of organic constituents of mixtures such as munitions that can provide quantitative concentrations to be used in fingerprinting. For example, in an application where the sampler contains 0.40 g EVA (and the detection limits of the mass spectrometry analysis are in the ng ml^{-1} range) compounds with a K_{EVA-W} on the order of 10^3 have water detection limits in ng L^{-1} and those with a K_{EVA-W} of $>10^5$ can be detected in the $<$ pg L^{-1} range. Of course the detection limits can be reduced by increasing the mass (and surface area) of EVA applied. (St. George et al, 2010)

Kinetics: From a kinetic perspective, the sampler measures the difference in chemical potentials of a compound across the water and EVA interface. Net movement continues until thermodynamic equilibrium is achieved or the sampling period is halted (Vrana et al., 2005). The exchange kinetics between sampler and water can be described by a first order one-compartment model:

$$C_{EVA}(t) = C_W k_1 / k_2 (1 - e^{-k_2 t}) \tag{3}$$

$C_{EVA}(t)$ is the contaminant concentration in the sampler polymer as a function of time, t, C_W is the contaminant concentration in the sampled medium (i.e., seawater, freshwater), and k_1 and k_2 are the uptake and offload rate constants respectively (Allan et al., 2006). Passive samplers follow one of two phases in the accumulation of organic pollutants during field deployments. These phases are kinetic or equilibrium and can be shifted by altering the sampler design (i.e. surface area and film thickness). The time to reach equilibrium for the EVA sampler is a function

of the partition coefficient K_{EVA-W}, medium and the uptake rates of the compound. Uptake follows a standard saturation curve that at equilibrium is reduced to:

$$C_W = C_{EVA}K_{EVA-W} \hspace{4cm} (4)$$

and K_{EVA_W} is the partition coefficient of the target compound at equilibrium. EVA samplers have been calibrated to determine K_{EVA-W} for a wide range of compounds including pesticides, flame retardants and explosives. For munitions compounds initial experiments have shown that EVA has a particularly high affinity that surpasses predictions based on the above equations though it is not clear if this is due to a high partition constant or due to a slower degradation of the TNT and RDX once within the film relative to the degradation rates in the surrounding environment. Unravelling this will also lend insight to offsets in detectable concentrations are measured in biota or sorbed to sediments though the dissolved concentrations decline rapidly.

Sampler Design: The sampler design is based on titanium, stainless steel or copper plates that are 5x10x0.1 cm for a total of 100 cm^2 surface coating area. Figures 2 a, b and c show variations of samplers that have been successfully deployed in the field. These include the traditional coated titanium plates (2a), EVA coated copper plates for stream sampling (2b) and EVA coated copper ribbon used for sampling to obtain vertical resolution in sediment porewaters. It is expected that sampler geometry in this project will be optimized to the target detection limits and the nature of the substrates being sampled. Currently samplers are deployed manually in shallow systems and have been diver deployed in deeper waters.

Figure 2 a) EVA samplers on titanium plates deployed in the Long Island Sound off the University of Connecticut's Central Sound Buoy b) EVA coated copper plates for stream sampling at EPA superfund site in Bennington, VT c) EVA coated copper ribbon used to obtain sediment vertical profiles in Sippewissett Salt marsh in Cape Cod, MA.

a)   b)   c)

Through ER2539 we have performed sufficient tests of the sampler to establish its efficacy in the field and propose to proceed to the next project phase following this SEED.

Tasks:

Hypothesis 1: EVA has a chemical potential for TNT, RDX and their derivatives that is equal to or greater than that of octanol. (Objectives 1 and 3)

Experiments were conducted to test uptake of the target compounds under both static and open steady state flow conditions to evaluate the differences in uptake curves and equilibrium partitioning constants for each compound. The uptake rates were evaluated as a function of contaminant concentrations to evaluate shift in equilibration times. Depuration rates were evaluated by placing spiked samplers in contaminant free systems (both static and open flow). The experimental set-ups are from our group's ongoing experiments (SERDP Project Number ER 2122) are described within as are all the analytical methodologies including high performance liquid chromatography (HPLC), gas chromatography mass spectrometry (GCMS) and isotope ratio mass spectrometry (IRMS) as summarized in St. George et al., 2010 and Smith et al., 2013, 2014.

Hypothesis 2: Target contaminants sorbed into the sampler are relatively stable and do not degrade over relevant deployment, retrieval and analysis timescales. (Objectives 2 and 3)

We conducted a time series of EVA samplers spiked with TNT and RDX (no derivatives) to evaluate the integrity of the sample over two week time intervals.

Hypothesis 3: The EVA samplers will yield comparable field concentrations to those measures with traditional extraction methods. (Objectives 3 and 4)

Two field deployments were conducted in Bedford Harbor, Nova Scotia (August 2015) and the Baltic Sea (September 2015). All samples were compared to traditional field samples of porewaters and sediments where each sampler was deployed, collected and extracted in the lab as per Smith et al., 2013.

Hypothesis 4: EVA samplers can be used for synoptic spatial mapping of TNT and RDX. (Objectives 3 and 4)

This Hypothesis was tested to a limited extend as field access was not possible for follow ups. There were spatial variations in the samples collected however which supported the mapping goals.

IV.   Materials and Methods

Chemicals:

EVA pellets were sourced from Sigma Aldritch (EVA 40%, 25% Acetate by weight) and Polysci (EVA 80%). Methylene chloride (DCM) acetonitrile and methanol UHP were purchased from Fisher Optima. The samplers and water samples collected were analyzed for TNT, RDX, and their respective breakdown products: 2A-DNT, 4A-DNT, hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), hexahydro-5-nitro-1,3-dinitroso-1,3,5-triazine (DNX), and hexahydro-3,5-dinitro-1-nitroso-1,3,5-triazine (MNX). 3,4-DNT was used as an extraction standard as it is normally a non-naturally occurring compound, and would not interfere with the elution of other compounds. Standards were purchased from Accustandard (3,4-DNT, 2A-DNT, 4A-DNT), SRI International (MNX, DNX, TNX, courtesy of Dr. Ronald Spangord), and China Lake NAWCWD (TNT and RDX, Courtesy of Dr. Steven Fallis).

Coating and Preparation of EVA Samplers:

Two grams of EVA pellets were dissolved per 100 milliliters of DCM, covered and stirred for two to four hours, or until full dissolution, depending on the percent acetate of the polymer (St. George et al. 2010). Substrates of stainless steel, as well as titanium, were used in this experiment, and maintained set dimensions of 5 x 7.5cm. The 'plates' were combusted at 450˚C, rinsed with acetone, and coated by plunging into the well-mixed DCM, then slowly pulling out and allowing time for the solvent to evaporate. This is repeated for a total of three times to get a uniform coating with a film thickness of about 7 µm. After preparation, samplers were wrapped in foil, placed into an airtight plastic bag, and refrigerated at 4˚C to minimize contamination from ambient air in the lab. Before exposure, these refrigerated plates were kept in their bags until reaching ambient room temperature.

Initial extracting methods of EVA Samplers:

The exposed samplers were dried (<30 min) via ambient evaporation in a fume hood, and placed into jars with ~200ml methanol as per St. George et al. (2009) the solvent was placed into a round bottom flask after 24 hours, capped, and another 200 ml aliquot of methanol was used for a second extraction. Both extracts were collected, spiked with an extraction standard of 3,4-Dinitrotolule, and concentrated via rotary evaporator (Buchi Rotovapor-R215) to ~ 5 ml. At this point, 15 ml acetonitrile was added. Rotary evaporation was carried out until only 5 ml of acetonitrile remained. Extracts were then transferred to snub-nosed vials, the round bottom flasks rinsed and collected with another 1-2 ml acetonitrile, and the collected fractions evaporated under a gentle stream of nitrogen to 1 ml. This was then transferred to a GC vial for analysis, refrigerated at 4˚ C until analysis via GC-ECD. The procedure was eventually replaced by the use of accelerated solvent extraction which reduced total extraction times to 2 h.

Water Sampling:

Concentrations of TNT and RDX in the water column were carried out using salting out procedures outlined by Miyares & Jenkins 1990, and modified by Ballentine et al. 2015. This

was performed by taking an aliquot of 4 ml seawater or milli-q (depending on experimental setup), then placing it into a 15ml Eagle tube preloaded with 1.5g NaCl and 1.5 ml of acetonitrile (Fisher Sci). The tubes were shaken, sonicated for ~10 minutes, and allowed to settle before the acetonitrile fraction was collected. Another extraction of the sample was done with 1 ml of acetonitrile, following the sonication and settling method as before. The second collected fraction was added to the first, and the solvent was concentrated under gentle stream of nitrogen until a final volume of 1ml was achieved. This was then transferred to a GC vial for analysis.

Uptake & Depuration Experiments:

For the uptake and depuration experiments, a 15L glass tank was filled with 10L of either milli-q, or sand filtered seawater from the Long-Island Sound (salinity of 34). Racks were placed into the tank to allow for full exposure to the water column, as well as ease of removal for extraction in solvent. For the uptake component of the experiment, all 22 plates (12 time points with duplicates, 24 plates total, 2 blanks) were placed into the same closed-system, munitions (TNT, 0.05 mg L^{-1} & RDX, 0.05 mg L^{-1}μM) spiked tank. Samplers were removed at set time points (0.5, 1, 2, 6, 24 h), with the remaining twelve samplers allowed to equilibrate for another 24 h before the depuration regime. At 48 h, 80 L of non-spiked water of the same type used for uptake was flushed through the system over 24 h at a rate of 3.3 Lh^{-1}. Once again, samplers were removed at set time points of 0.5, 1, 2, 6, and 24 h, and all samplers were extracted as outlined above.

Equilibrium Partitioning as a function of Temperature & Differing EVA Types:

For the varying percent acetate EVA experiment, samplers of each EVA25, EVA40, and EVA80 were coated in triplicate, placed into 250mL glass jars with a spiked TNT and RDX milli-Q solution. Blanks were produced using the same coating protocol as before, and placed immediately into solution when the experiment started. After six hours of exposure, the samplers were removed, and allowed to dry in a fume hood. Extraction procedures were followed as outlined above. This experiment was then reproduced at 25, 14, and 4 ˚ Celsius.

Analysis:

Analysis was carried out on an Agilent 7890A gas chromatography/electron capture detector unit (GC/ECD). The method was originally described by Pan et al. (2005), with modifications by Smith et al. (2013) and Ballentine et al. (2015). A 1 microliter aliquot of solution was injected in pulsed/splitless mode into a double taper pulsed/splitless liner. Helium (Airgas, UHP HE300) was used as a carrier gas, and the flow rate was set to 11.9 ml min-1, and the column used for this analysis is an HP-DB5 column (30m x 320 µm, 0.25 µm, Agilent). Oven temperature was set to hold at 90˚C, with two ramps over the course of 14 minutes. Ramp one was 10.9 minutes, starting at 90˚C, and held for 1.5 minutes once reaching 200˚C. Ramp two was 14.2 minutes for 200 ˚C to 250˚C, and was held for 1.9 minutes. An external calibration curve containing TNT, RDX, 2A-DNT, 4A-DNT, 3,4-DNT, TNX, DNX, and MNX was used for quantification, and the reporting limit for the compounds was 0.7 ng ml^{-1}.

Field Tests:

The first field test was conducted in Bedford Harbor in August 26-29, 2015 (Figure 3) with the official authority of John McCallum, Royal Military College of Canada and the services of Terry Long, Wentworth Environmental Inc. The harbor contained several visible UXOs in relatively shallow waters and the samplers were placed in triplicates (in stainless steel cages) by rope within 1 m of the UXOs. Each cage was tethered to a floating marker and retrieved the same way 48 hours later. Bottom water samples were collected using 5 L Niskin bottles at both deployment and retrieval times. Sediment samples were collected by grab sampler where possible within the 1 m radius from the UXO. Collectively 3 sites (one shallow control, H0 and two UXO sites H1 and H2) were successfully sampled.
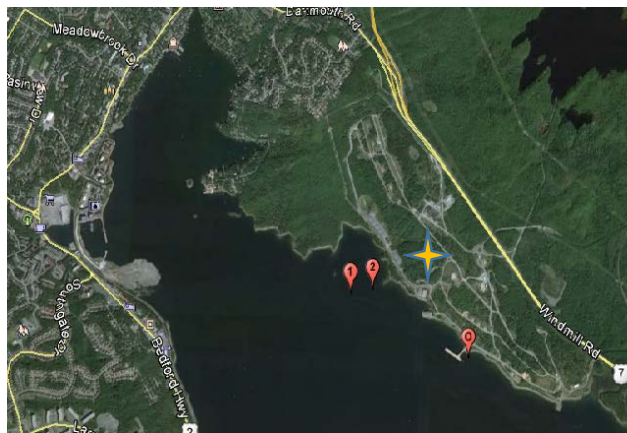
Figure 3: Sampling locations in Halifax Canada, Bedford Basin. The star depicts the location of the Military Base. Markers 1 and 2 depict station H1 (44°42'36.64"N, 63°38'41.57"W) and H2 (44°42'37.52"N, 63°38'33.22"W) while marker 0 depicts station H0 (44°42'22.10"N, 63°37'57.00"W) the shallow, tidally flushed control site.

The second field deployment took place in the Baltic Sea (September 23 -28, 2015) through a collaboration with the NATO funded MODUM project and the permission of Terry Long, IDUM and Jacek Bedowski Lead PI of MODUM. Here the samplers were placed at two stations shown in Figure 4 at the CHEMSEA project's Gdansk Deep dumping site. Samplers were deployed by rope at station B1 at 97 m and at station B2 which was 101 m deep. Samplers at station B1 were retrieved however, samplers at station B2 were left in the field due to ROV failure. In a follow up cruise conducted in March 2016 Bedowski's group was able to locate the sampling cages and retrieve them. They have been sent for shipping to our laboratory for analysis. These will yield results of a 6 month deployment and will be analyzed for a wide spectrum of munitions compounds including dichlorodiethyl sulfide (mustard gas).
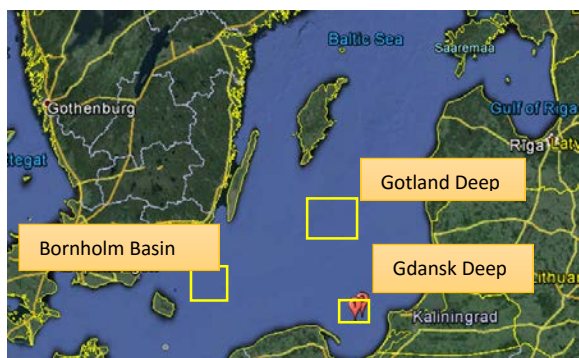
Figure 4: Baltic, Gdansk Deep sampling sites B1 (recovered during original cruise) (54°51'16.75"N, 19°10'22.36"E) and B2 (recovered in March 2016) (54°54'28.89"N, 19°21'13.06"E). Yellow squares depict known dumping sites evaluated in the CHEMSEA Project.

V Results and Discussion:

Uptake and Depuration Rates:

The concentration of munitions sorbed by the sampler increase rapidly over the first two hours of the experiment for TNT and RDX in both milli-q and saltwater systems. Under these sampler geometries and film thicknesses (approx. 7 µm), steady state was reached in under 6 hours (Figure 5). Uptake was fastest in artificial seawater followed by freshwater and finally by natural seawater. The differences in uptake between artificial and actual seawater are attributed to competitive sorption between dissolved organic matter (at 160 µMC) and the sampler. This difference in uptake does not influence the deployment time but does have an impact of the quantification of water and porewater concentrations. That is the samplers will equilibrate with the truly dissolved concentrations of munitions. Further investigation is warranted here to establish an algorithm that includes the attenuation of dissolved organic carbon in sampler uptake and in estimating total field concentrations accurately. Table 1 summarizes the 6 hour uptake rates.
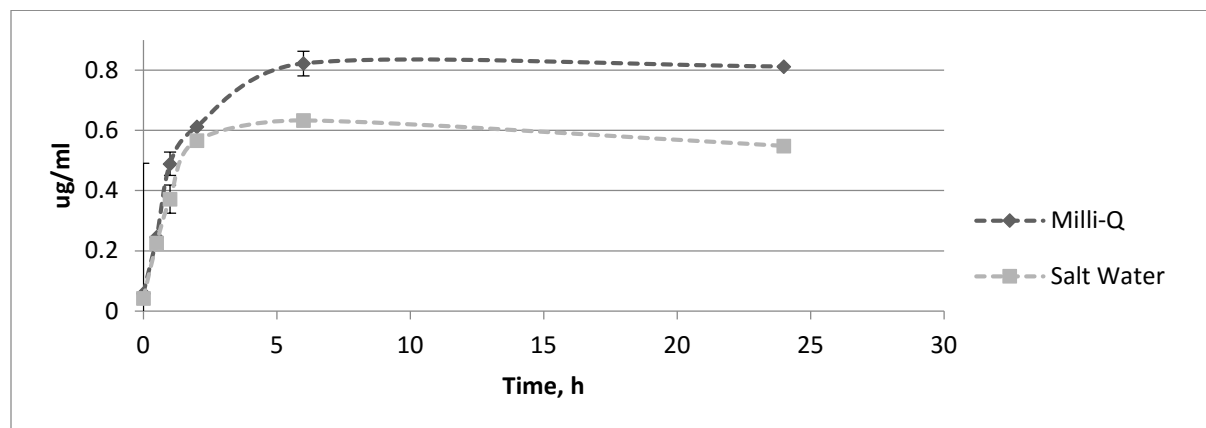
Figure 5a: EVA (µg ml^{-1} extract) uptake curves for TNT in milli-Q and natural seawater 40% EVA
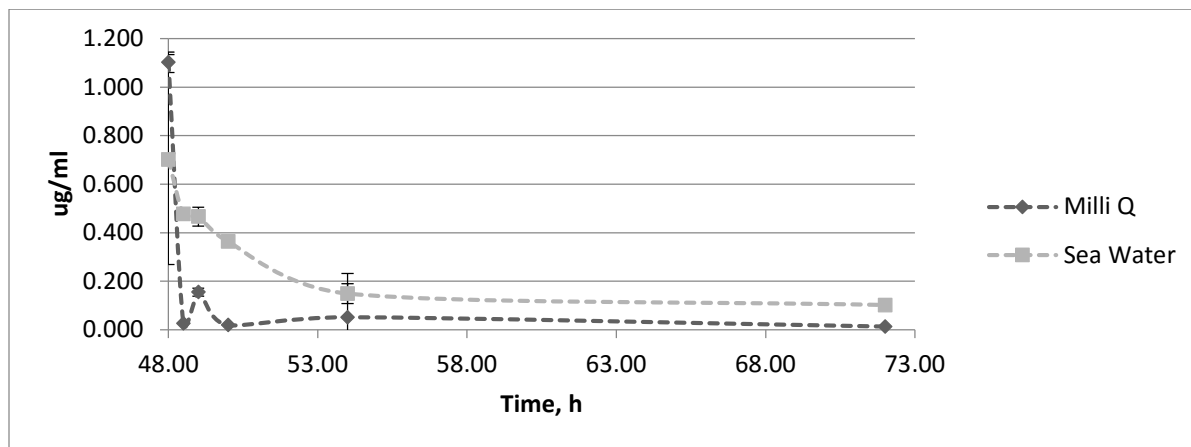
Figure 5b: EVA (µg ml⁻¹ extract) depuration time series of TNT in an open flow system in 40% EVA.

After remaining in the spiked solution in the tank for another 24 hours, the tank was flushed with un-spiked solution at a rate of 3.3 Lh⁻¹. These results are summarized in Table 1. Within the first two hours, the amount of TNT in the plates decreased from 1.103 µg ml$_{EVA40}$⁻¹ to 0.019 µg ml$_{EVA40}$⁻¹, an 82% reduction, and then retained 0.013 µg ml⁻¹ for the remaining 22 hours. TNT in natural seawater reached a 79% loss of sorbed munitions; 0.702 µg ml$_{EVA40}$⁻¹ to 0.149 µg ml$_{EVA40}$⁻¹ after six hours, though the initial depuration occurred at a slower rate than the milli-q depuration. Thus in marine systems uptake is faster and depuration is slower to/from the EVA samplers relative to freshwater systems.

The concentration of RDX in the samplers from the milli-q tank showed an 86% reduction in concentration at the two-hour time point, going from 0.14 µg ml$_{EVA40}$⁻¹ to 0.02 µg ml$_{EVA40}$⁻¹. For the RDX seawater experiment, a 51% reduction in concentration was measured after two hours. The starting concentration of 0.057 µg ml⁻¹ was reduced to 0.024 µg ml$_{EVA40}$⁻¹ at 24 hours. Table 1: Uptake, depuration rates and steady state partitioning of target compounds TNT and RDX at steady state in three water types.

Table 1: Summary of uptake and depuration rates for TNT and RDX at 24 °C for different water types spiked to 0.05 mg L^{-1} of munition (using EVA40)

	TNT			RDX		
	Milli-Q (0 gkg^{-1})	Artificial Seawater (30 gkg^{-1})	Actual Seawater (34 gkg^{-1})	Milli-Q (0 gkg^{-1})	Artificial Seawater (30 gkg^{-1})	Actual Seawater (34 gkg^{-1})
k_1 (h^{-1})	2.13	NA	2.17	1.13	NA	0.94
k_2 (h^{-1})	0.48	NA	0.30	0.42	NA	0.36
$logK_{EVA-W}$	2.14	2.10	2.04	1.44	1.55	1.34

Storage Integrity

In order to determine the sample integrity EVA samplers that had been equilibrated at concentrations equal to those in the uptake experiments were wrapped in aluminum foil, placed in zip lock bags and stored at 4°C. The samplers were extracted every two weeks for three months to monitor changes due to storage (12 weeks). The first detectable changes in concentrations appeared at 12 weeks for TNT ($< 5\%$) though RDX remained at its original concentrations. Thus EVA samples retrieved from the field are stable if refrigerated in air tight packaging for up to three months. It is expected that if frozen samplers can be stored longer though this will be confirmed in future work.

Comparison of Relative Uptake Rates for EVA 25/40/80

The EVA co-polymer is composed of different ratios of ethylene and vinyl-acetate groups. As the composition of the polymer changes, so does its density and polarity. The differences in the polymers also result in different coating properties. The 25% EVA form has thermoplastic properties and results in an adhesive, sticky coating surface, as does the 40% EVA, while the 80% EVA produces a smooth, matte surface once it is coated.

Table 2: Properties of the different % acetate EVA where. x refers to ethyl- and y acetate molecular coefficients as per Figure 1.

% Vinyl acetate	x	y	Polarity ratio	MW per unit gmol^{-1}	Density gml^{-1}	Elasticity	Melt Temp ˚C
25	9	1	1:10	338	0.948	Hard	75
40	9	2	2:11	424	0.986	Malleable	60
80	3	4	4:07	428	NA	Powder	NA

The amount of TNT and RDX taken up by the samplers varies with temperature and composition of the polymer. Figure 6 offers a visual representation of the data from Table 3, grouped by EVA type and compound. The EVA80 sampler was the most efficient over all temperature ranges for these target munition compounds. Compared to EVA80 at 25˚C, EVA25 only took up 25% of the TNT and 9% of the RDX, while EVA40 sorbed 48% of the TNT and 31% of the RDX that EVA80 was able to per gram EVA. In the 14˚C experiment, EVA25 sorbed 41% of the TNT and 11% of the RDX that EVA80 did, while EVA40 sorbed 55% and 34% of TNT and RDX, respectively. The 4˚C experiment yielded uptakes of 34% TNT and 11% RDX for EVA25, with 76% TNT and 28% RDX uptake for EVA40 relative to EVA80's sorbed concentrations.
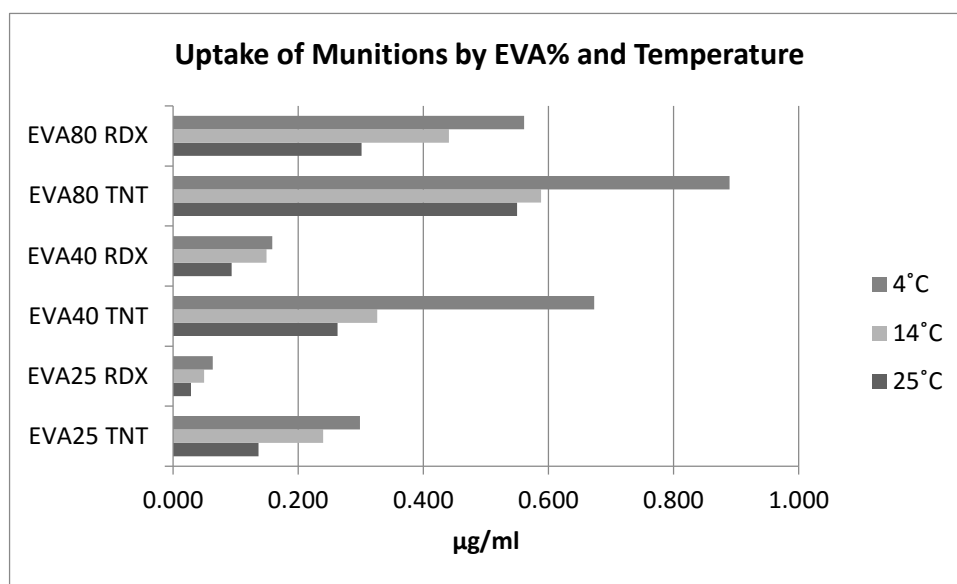
Figure 6: Equilibrium uptake values of TNT and RDX on plates for three temperatures and three EVA film types.

Table 3: Uptake of munitions by EVA25, EVA40 and EVA80. Concentrations represent amounts extracted by a designated average mass of EVA for samplers at equilibrium with 0.05 mgL^{-1} solutions.

Temp. °C	EVA Type	Avg g EVA	TNT (µg ml^{-1})	RDX (µg ml^{-1})	LOG K$_{EVA}$ TNT	LOG K$_{EVA}$ RDX
25	EVA25	0.062	0.159	0.033	1.71	1.04
14	EVA25	0.073	0.289	0.060	1.97	1.28
4	EVA25	0.074	0.367	0.078	2.00	1.32
25	EVA40	0.030	0.149	0.053	2.00	1.56
14	EVA40	0.025	0.157	0.072	2.10	1.75
4	EVA40	0.032	0.365	0.086	2.35	1.73
25	EVA80	0.066	0.668	0.377	2.32	2.06
14	EVA80	0.068	0.773	0.580	2.35	2.23
4	EVA80	0.073	1.077	0.679	2.47	2.27
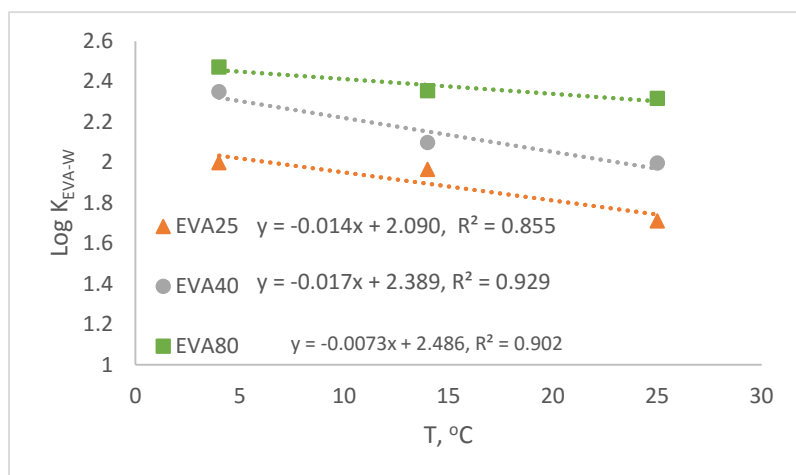
Figure 7a: TNT Uptake Kinetics as a function of EVA type and temperature
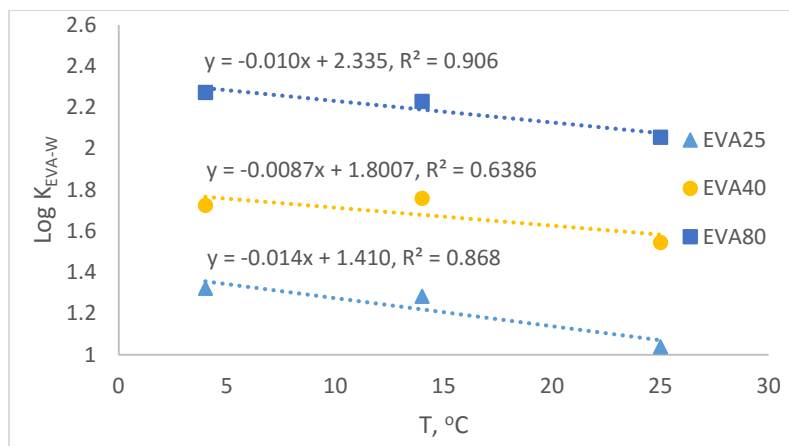
Figure 7b: RDX Uptake as a function of EVA type and temperature

The log K_{EVA-W} values for the temperature experiment, seen in Fig 7a (TNT) and b (RDX) show reasonable linearity for both compounds across all EVA types. There is clearly an inverse effect of temperature on the equilibrium concentrations in the range of a 0.01 reduction in $LogK_{EVA-W}$ for TNT and RDX per unit increase in °C. EVA80, as the most polar film, is slightly less sensitive to temperature changes alluding to the role of the acetate groups in sorption.

Table 4: Uptake of munitions derivatives by EVA25, EVA40 and EVA80. Concentrations represent amounts extracted by a designated average mass of EVA for samplers at equilibrium with 0.05 mgL^{-1} solutions of parent compounds.

Temp.°C	EVA type	gEVA	MNX (µg ml^{-1})	DNX (µg ml^{-1})	TNX (µg ml^{-1})	4-ADNT (µg ml^{-1})	2-ADNT (µg ml^{-1})
25	EVA25	0.062	0.012	0.136	0.017	0.040	0.011
14	EVA25	0.063	0.016	0.090	0.025	0.017	0.042
4	EVA25	0.074	0.019	0.078	0.028	0.040	0.047
25	EVA40	0.030	0.014	0.127	0.021	0.033	0.018
14	EVA40	0.025	0.013	0.069	0.024	0.027	0.027
4	EVA40	0.032	0.016	0.140	0.024	0.080	0.047
25	EVA80	0.066	0.012	0.087	0.037	0.057	0.050
14	EVA80	0.068	0.014	0.116	0.041	0.087	0.077
4	EVA80	0.073	0.014	0.108	0.032	0.098	0.081

Table 4 illustrates the advantage of a non-specific sampler and the ability of the EVA sampler to assess breakdown products of the target precursors simultaneously. Derivatives of RDX, MNX, DNX and TNX did not show a preference for film type though there was slight increases of TNX uptake in EVA80. TNT derivatives did show a slight preference for EVA80 and consistent inverse trends with temperature. Follow up studies focusing on isolated treatments of these compounds are warranted.

As can be seen in Figure 8a&b, increasing salinity had a lesser effect on the amount of munitions sorbed by the sampler. The K_{EVA-W}'s of the munitions increased with salinity, due to the change in ionic strength of the system and salting out effects.

a)
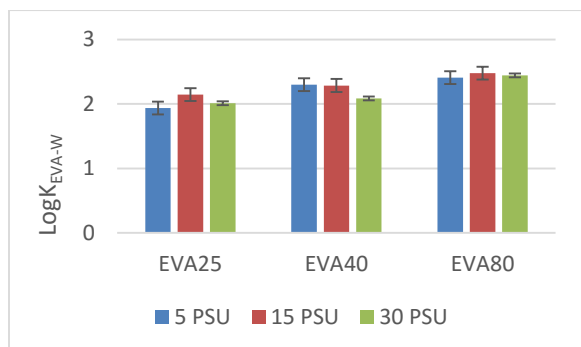
b)
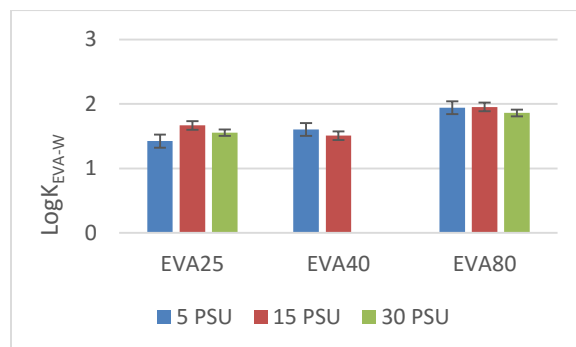
Figures 8a and b: Effect of salinity on the LogK$_{EVA-W}$ among EVA types.

Figures 8a and b illustrate that for a given EVA type, salinity has no significant effect on equilibrium partitioning. The increases in Log K$_{EVA-W}$ based on the polarity of the EVA monomer again appear clearly in this data.

Utilizing the equilibrium constants derived from the K$_{EVA-W}$ values reported in Table 3, the associated change in free energy equation of sorption for compounds in the various EVA films may be quantified and the data seem appropriate for the application of linear free energy models. This will be addressed in both the publications arising from this study and in future work. A linear regression on the equilibrium constants for both TNT and RDX, versus T^{-1} as the independent variable gives a Y-axis intercept of ($\Delta S°/R$), and a slope of ($-\Delta H°/R$). By multiplying by the thermodynamic constant (R) of 8.314 J mol^{-1} K^{-1}, values for enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be calculated and grouped by EVA type.
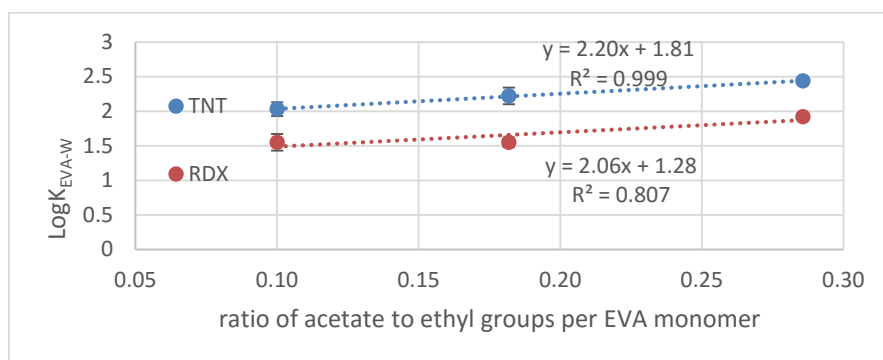
Figure 9: Linear free energy relationships for TNT and RDX per EVA monomer polarity.

The lowest % acetate polymer in this study, EVA25, was able to sorb both TNT and RDX, although in much lower amounts than the EVA40 and EVA80 given the same time periods. As the amount of acetate in the polymer decreases, the relative amount of RDX able to be sorbed also decreases. Due to the change in polarity of the polymer as a whole, the less polar RDX is unable to sorb in the same manner as the more polar TNT.

Coating of substrate with the EVA25 polymer has its own set of issues. The hard, opaque beads do not respond well to solvents without adding heat to the mixture, and allowing it to sit for up to 48 hours before full solvation occurs. The film integrity is also variable, as the higher concentration of ethylene within the mixture results in a less pliable coating that cannot stretch as well as EVA40 when temperature decreases, resulting in some peeling of the polymer from the substrate after 24 hours of exposure.

The EVA80 admixture, due to its dispersive properties and additives, is more difficult to dissolve into halogenated solvent, but is equivalent to the other EVA types in regards to blanks and control samples. It was shown that this mixture was the most effective at sorbing the nitrogen containing munitions, but due to its resistance to solvation by volatile solvents, it should be used only when preliminary work utilizing EVA40 or SPE has detected the presence of compounds of interest. While it retains some thermoplastic properties of the lower percent acetate mixtures, it does not seem to readily contract or expand as the EVA40 mixture does.

EVA40, the more thoroughly studied of the polymers in this experiment, was able to sorb TNT and RDX more readily than the EVA25 sampler. Much like the EVA25 sampler, RDX was not concentrated as efficiently as TNT, (though significantly more efficient that octanol) likely due to differences in polarity between the molecules and the frequency of the polar acetate group present. In light of this, use of the EVA40 sampler is an all-around best choice for its coating ease, film thickness, film integrity, how readily it dissolves in relatively un-harmful solvents (DCM, Hexane/Ethyl-acetate mixtures, etc), thermoplastic properties, and chemical affinities. The film integrity from the EVA40 samplers was retained across the different temperatures, as the higher concentration of acetate present allows for a higher amount of deformation due to thermoplastisic contraction. For all intents and purposes, EVA40 should be considered a useful middle ground, and should be used for exploratory work in which a wide range of compounds might be present.

Field Deployments: Bedford Harbor, Halifax Nova Scotia

Table 5 summarizes the results from the first field deployment. In order to help optimize the samplers both equilibrium thin film and non-equilibrium thick film (integrative versions) were used. It was intended that for low concentrations the integrative version could yield lower detection limits. Both sites H1 and H2 gave positive results for RDX and TNT and both ADNT (amino,dinitrotoluenes) derivatives of TNT. This is expected as TNT is known to degrade significantly faster than RDX to ADNTs. It is also noteworthy that no compounds were detected at H0 the tidally flushed shallow site that was away from the UXOs. This field deployment yielded values that were consistent with traditional water extraction methods though the passive sampling technique was remarkablty simpler and able to detect lower concentrations without the need of extracting cumbersome extraction volumes. Though the sampling scope was modest, the samplers yielded concentrations that were consistent with those from the SANDIA report by Rodacy et al. (2001). In addition to our target compounds, samples were sent to ALS analytical which is an EPA certified laboratory in order to confirm our results. ALS detected significant concentrations of our target compounds in addition to pentaerythrotol tetra nitrate (PETN), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (OTT), nitroglycerine (NG), 2,4,6 trinitrophenylmethylnitramine (Tetryl). Again the broad uptake efficiency of the EVA samplers was confirmed. It should be noted that these compounds were completely below detection in the SANDIA repot and that these were obtained in 2 to 5 g of film in 24 and 48 hours.

Table 5: Halifax, Nova Scotia. Bedford Harbor - Station details and concentrations (Rodacy et al., 2001)

Station H1 (n=2)	UCONN GC-ECD $\mu g \ ml^{-1}$	ALS HPLC-PD $\mu g \ ml^{-1}$	Estimated Water Concentrations $\mu g \ L^{-1}$	Reported Concentrations $\mu g \ L^{-1}$
MNX	0.022-0.025	--	0.1	--
DNX	0.014-0.017	--	0.1	--
RDX	0-0.093	0-0.0076	0 - 0.4	--
4aDNT	0.027-0.049	0.011-0.012	0.1-0.2	0.97-3.97
2aDNT	0.098-0.403	0.0053-0.0082	0.5-2	0.64-3.92

2,4-DNT		0.0034-0.0067		0.05-0.40
4-NT		0.0030-0.0060		--
1,3,5-TNB		0.0047-0.031		1.24 (0-800)
1, 3-DNB		0.0032-0.0050		--
Tetryl		0.0021-0.0057		--
NG		0 - 0.23		--
OTT		0.0031-0.0046		--
PETN		0.012-0.033		--

Baltic Sea

Baltic sample bundles were deployed at two sites. Both were at a known UXO dumping site described above. Values are summarized in Table 6. These samples were extracted and analyzed in both our lab and externally by an ALS lab for verification. Both target compounds were detected on the samplers that were deployed for 48 hours. Station B2 was not retrieved during the cruise due to equipment failure (ROV) however a follow up cruise in March 2016 has retrieved these samples and they will be analyzed shortly. Dr. Paula Vanninen who is the director of VERIFIN – The Finnish Institute for Verification of the Chemical Weapons Convention at the University of Helsinki is collaborating with us to examine a wider range of munitions captured by the sampler. This is an exciting follow up that has emerged from the MODUM opportunity.

During the CHEMSEA efforts , an intercalibration between three analytical groups found significant differences in results thus actual concnetrations were not reported. Positive identifications were made for at least one compound in 10 of 30 samples retrieved from Gdansk Deep. Again the utility of the EVA samplers yielding several compounds in one deployed site is evident. We look forward to the results from B2 and from our collaborations.
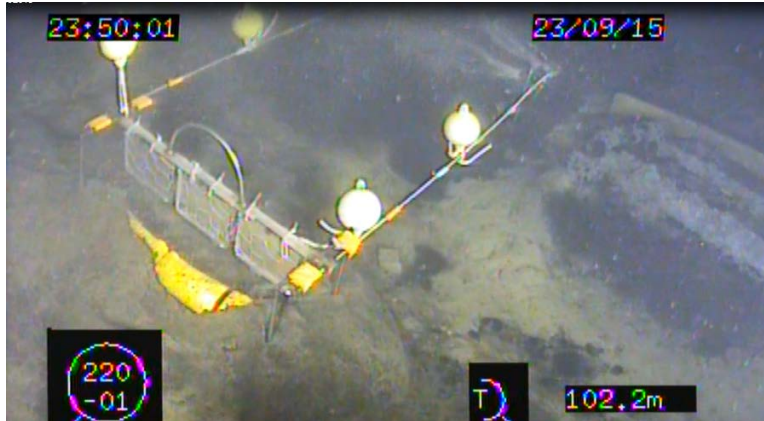
Figure 10: ROV image of sampler frame at station B2 (retrieved March 2016)

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Table 6: Baltic Sea- Identified compounds at Gdansk Deep station B1 and concentrations where appropriate.

		UCONN/GC-ECD	ALS/HPLC-PD	Water Conectrations	Reported C0ncentrations
Station		ug ml-1		ug/L	
B1 (n=**4)**	MNX	0.03-0.13	ND	0.2 -1.0	
	3,4 DNT	0 - 0.018	ND	0 - 0.01	
	DNX	0.002-0.012	ND	0.01 - 0.2	
	TNT	0-0.070	.0025-.0046	0 - 0.04	
	TNX	0-0.468	ND	0 - 2	
	RDX	0-0.093	0-0.043	0 - 0.6	
	4ADNT	0-0.092	0.051-0.069	0 - 0.6	
	2ADNT	0.001-.004	0-0.0071	0.005-0.02	
	tetryl		0.003-0.009		
	NG		0.016-0.021		
	OTT		0-0.014		
	PETN		0.075-0.35		

VII.   Conclusions and Implications for Future Research

This project has conducted the necessary calibration experiments to evaluate EVA sampler uptake under various salinity and temperature conditions that are essential in interpreting field samples. Critical uptake, depuration and time to equilibrium/steady state were determined to optimize field deployment times. A noteworthy result that was not expected was the significant influence that competitive sorption could have on the released munitions in aquatic systems. Future work is required to further evaluate the degree to which dissolved organic matter in bottom waters and porewaters could alter the sampler uptake efficiency. The extraction procedure was improved to by incorporating accelerated solvent extraction. Total extraction to analysis time is now 2 hours per sample (10 min extractions and 1 hour solvent reduction) and it is likely this can be further optimized. These methods can be integrated into one simple operating procedure. Our ultimate goal in this project was to show proof of concept for the utility of these samplers in natural marine systems at environmentally relevant concentrations. The samplers have successfully detected munitions that include derivatives and a wider range of energetic compounds than was expected. The samplers have yielded concentrations in agreement with those of previous surveys at the same sites and were able to improve on the amount of compounds detected and the detection limits. We propose to further test the samplers in areas of identified concern and to evaluate the efficacy of EVA as a remediation tool at targeted areas where leakage has been identified. Our collaboration with Dr. Vanninen who is a global expert on chemical munitions analysis will help expand on the utility of these samplers for a broader range of compounds and their derivatives in aqueous systems. The results of ER2539 have produced sound justification for a broader and larger scope project that can include intensified sampling and mapping including the potential for remediation. Objectives for the large scale effort include:

- How does the sampler perform in a range of sediments and redox conditions?
- How do natural ranges of dissolved organic matter influence the sampler?
- What is an appropriate spatial and temporal resolution for mapping of TNT, RDX and their derivatives in the field?
- Can the sampler be segmented to provide sediment depth profiles and at what resolution?

- Can an EVA coated mesh be used in sediment systems for remediation?

- Does impregnating the EVA with a carbon resin shift the sorption and remediation properties?

- Further optimization of the methodologies and development of standard operating procedures

- How do the optical properties of the EVA film change when it has sorbed the target compounds? (this is to assess potential for real time monitoring)

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IX. APPENDIXES
Appendix A: SEED reports for project period 2015/2016

ER2539 APPROVAL DATE: 04/26/2015 End Date: 04/23/2016

TASKS/SUB-TASKS:

GO/NOGO	TASK	START YEAR	PLANNED COMPLETION
	1. Establishing the chemical potential of ethylene-vinyl Acetate for TNT and RDX: Experiments will be conducted to test uptake of the target compounds under both static and open steady state flow conditions to evaluate the differences in uptake curves and equilibrium partitioning constants for each compound. The uptake rates will be evaluated as a function of contaminant concentrations to evaluate shift in equilibration times. The experimental set-ups are in place from our group¿s ongoing experiments (SERDP Project Number ER 2122) as are all the analytical methodologies including high performance liquid chromatography (HPLC), gas chromatography mass spectrometry (GCMS) and isotope ratio mass spectrometry (IRMS) as summarized in St. George et al., 2010 and Smith et al., 2013, 2014. Depuration rates will be evaluated by placing spiked samplers in contaminant free systems (both static and open flow).	2015	12/2015
	2. Assess the stability of target compounds within the sampler film: We will conduct a time series of EVA samplers spiked with TNT and RDX (no derivatives) to evaluate the integrity of the sample over two week time intervals. These tests will be conducted in a closed equilibrium system that is completely aqueous and in sediment porewaters. In order to differentiate between breakdown products derived from the sampler and those from sediments we will use isotopically labeled TNT and RDX for the depuration compounds and unlabeled compounds in the ambient environment. These will be quantified as above by GCMS and IRMS.	2015	02/2015
	3. Field deployment of samplers and comparison with traditional sampling: One field deployment will be conducted with at least 10 samplers in representative sediment types/locations. All will be compared to field samples of porewaters and sediments where each sampler was deployed, collected and extracted in the lab as per Smith et al., 2013. Should good agreement be found (correlated at over 85%) the traditional sampling will be reduced in field trials 2 and 3 (fewer traditional sampling checks), otherwise both sampling methods will be conducted for all samples and sights.	2015	03/2015
	4. Synoptic spatial mapping of TNT and RDX: The second and third field studies will include a broader spatial deployment of the samplers to provide information for a broader future effort. These will be impregnated with isotopically labeled TNT and RDX in order to assess in-field depuration rates and assess sampler performance. These depuration compounds will also help assess variations in sampler performance in various field conditions. Porewaters will be characterized in the field for temperature, salinity, pH, REDOX and oxygen concentrations using a UNISENSE system for the top 10 cm of sediment which is the depth the samplers will be exposed to. Sediment samples will be collected for traditional extractions and for elemental analysis in order to quantify organic carbon content and potential competitive sorption.	2015	09/2015
	5. Reporting:	2016	05/2016

	5.1 Final Report	2016	02/2016
	5.2 Final Debrief	2016	05/2016

FUNDING HISTORY AND OUTYEAR ESTIMATES:

FY	Proposal Requested ($K)	Planned ($K)	Total Amt Distributed ($K)
2014	$0.000	$40.000	$40.000
2015	$147.698	$107.698	$107.698
TOTAL	$147.698	$147.698	$147.698

FINANCIAL STATUS (Non-Expended Years):

FY	Date Funds Received	Last MFR	Expenditures		
			Planned ($K) as of Jan-16	Actual ($K)	% Expd of Amt Distributed
2015	04/24/2015	Jan-16	107.698	103.605	96.200

SUBMITTED ACTION ITEMS:

Type: IPR

Due Date: 06/15/15
Status: SUBMITTED
Action item: Please plan on providing a white paper by June 16, 2015 that addresses the questions and comments from the Sediment Review Panel, bulleted below. Recognizing that this project is a SEED project, and is just getting underway, we are not expecting definitive answers per se, but rather, how this program will address these items. 1. Please discuss further how you plan on demonstrating utility of ethyl vinyl acetate (EVA) samplers in remedial site assessments. It is not clear how time-weighted measures of RDX and TNT can be helpful to managing munitions-contaminated sites. Slide 11 (in the pdf made available to the SRP) shows a very quick plate uptake for RDX and TNT (less than 5 hours), but a somewhat slow depuration rate (Slide 13). Slide 14 presented an exchange kinetic equation. These are all based on lab water exposures. The questions that the SRP is interested in are (a) how you will compare time-weighted measures of EVA-exposed sediments to actual porewater/ groundwater measures of TNT/RDX, (b) how would you envision a sampling strategy in a tidal-influenced environment, and (c) how you envision this tool being used to inform remedial requirements ¿ other than simply indicating presence/absence of TNT/RDX (i.e., in a risk assessment) 2. There is some concern about the sampler construction and the durability of the EVA film in sediments. Regarding the sampler, please discuss whether it is necessary to use titanium ¿ an expensive material. Copper plates were shown during the Norfolk presentation, but we suspect those might not be sustainable over numerous sampling events. Could anodized aluminum, for example, be an alternative substrate? What has been done, or will be done, to confirm that EVA can withstand being pushed deep (e.g. 30 cm) into different sediment types and remain intact (i.e., not peal or tear off the sampler)? 3. Presuming a successful demonstration, the Program will be interested in having a Standard Operating Procedure for making, placing, and analyzing these EVA samplers. Please see, for example, the SOPs developed for ER-200915. 4. Please consider how you will develop sampler costs for construction and analysis. Slide 20 appears to suggest that this technology will be proprietary and handled through EVA Systems LLC. With a successful SEED demonstration, and if further funding is provided by the Program, we would look for this technology to be transferable to all potential users (i.e., others to be able make and deploy these samplers), as well as to have the analyses demonstrated at a commercial laboratory.
PI Response: Please note that the white paper has been emailed as of May 26, 2015.

PENDING ACTION ITEMS:

ACTION ITEMS COMPLETED FOR THE LAST 14 MONTHS:

OBJECTIVE: This project seeks to conduct necessary calibration and sensitivity tests of a passive thin-film equilibrium sampler using ethylene vinyl acetate (EVA) for optimization and deployment in sediments of active and legacy artillery ranges to detect and remediate target munitions compounds 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and their derivatives). Specifically:

Objective 1: Evaluate EVA sampler uptake and offloading rates for the target munitions compounds as a function of ambient concentration and film thickness.

Objective 2: Assess the stability of target compounds within the sampler film for deployment timescales.

Objective 3: Optimize sampler geometries and film thicknesses for the detection of target field concentrations (below nanograms per liter).

Objective 4: Deploy sampler onsite to demonstrate mapping field distributions of target compounds and identifying accumulation zones.

APPROACH: This project involves laboratory calibrations of the target compounds TNT, RDX and their derivatives followed by a series of on-site field tests. Laboratory calibrations are used to determine variations in sampler uptake kinetics over a range of film thicknesses and field concentrations. This will include uptake and depuration rates. Integrity of the compounds within the EVA film over relevant deployment timescales will be determined in order to optimize deployment times and sampling protocols. Laboratory experiments will be used to design and plan for field deployments. Three field deployments will include 1) determination of on-site uptake and offloading rates through the use of isotopically labelled performance reference compounds 2) compare sampler concentrations with traditional sampling methods. Three are requested in order to enable iterative feedback and optimization. Field studies will also test the sampler?s efficacy as a concentration mapping approach to assess the resolution and limitations in the field.

TASKS/SUB-TASKS:

GO/NOGO	TASK	START YEAR	PLANNED COMPLETION	REVISED COMPLETION	ACTUAL COMPLETION
	1. Establishing the chemical potential of ethylene-vinyl Acetate for TNT and RDX	**2015**	**12/2015**	**07/2015**	**06/2015**
	2. Assess the stability of target compounds within the sampler film	**2015**	**02/2015**	**07/2015**	**07/2015**
	3. Field deployment of samplers and comparison with traditional sampling	**2015**	**03/2015**	**10/2015**	**08/2015**
	4. Synoptic spatial mapping of TNT and RDX	**2015**	**09/2015**	**01/2016**	**09/2015**
	5. Reporting	**2016**	**05/2016**		
	5.1 Final Report	2016	02/2016		
	5.2 Final Debrief	2016	05/2016		

PROGRESS PAST QUARTER/CONCERNS:

2016 July

Progress Past Quarter

No Progress Past Quarter Reported For This Quarter

Concerns

No Concerns Reported For This Quarter

2016 April

Progress Past Quarter

Progress Past Quarter: -completed Analysis of field samples
-completed external lab verification of samples
-established more efficient methods for extraction
-began a softer fragmentation technique for the analysis of derivatives in field samples using negative chemical -
-ionization
-preparing final report with intent to submit proposal for future work

Concerns

No Concerns Reported For This Quarter

2016 January

Progress Past Quarter

Progress Past Quarter: Our project is now complete and we are preparing our final report for submission. We expect to have our final report submitted the first week of March.

Concerns

No Concerns Reported For This Quarter

2015 October

Progress Past Quarter

Progress Past Quarter: The second quarter of this project was dedicated to accessing sites where munitions have been detected in the past. With the help of Harry Craig from the EPA and Charles Coyle from USACE we were able to get access to a site outside of Bedford Harbor, Halifax Nova Scotia, Canada for a short two day (Aug 29-31) deployment in very shallow sites (under 2 m) where unexploded ordnances (UXOs) were readily visible. The site also experiences regular military drills and therefore frequent re-exposure. Our samples were run for the entire set of compounds in EPA method 8330 and preliminary results indicate matches for RDX, and two TNT derivatives (2,4 and 2,6 DNT). These samples are currently being completed and quantified.
Our second sampling opportunity came in September in the Baltic sea where we joined the NATO SPS MODUM cruise which was sampling at known UXO dump sites. The cruise occurred from Sept 17 to 27 and three sites were sampled. One set of samplers has been retrieved and is currently being extracted. Two more sampler sets remain in the water due to retrieval limitations and the chief scientist is planning on retrieving them and sending them to us over the next 30 days. We also sent a sampler set to Sweden in July of 2015 which was deployed by Anders Ostin and the Swedish Military however we were informed that the sampling area had been trolled by fishermen and the samplers were missing. Our preliminary results are very promising and we would like to accept any sampling opportunity in areas of concern as they arise. In the mean time we continue to finalize quantification of our field samples.
From a methodological perspective we have refined our extraction procedure using a pressurized liquid extractor and our sample processing has been reduced to a 10 min extraction followed by solvent reduction and sample preparation. In summary a sample can be analyzed from start to finish within two hours of arriving to the lab. This has of course streamlined the process considerably. Our intent is to now incorporate this improvement in a standardized operating procedure to be included in the final report.
The project has resulted in two presentations in Hamburg, Germany (May 2015) at the NATO SPS MODUM meeting and Aarhus, Denmark (October 2015) at the 3rd International Conference of Environmental Monitoring and Assessment (http://dce-conference.au.dk/). We are now working on the draft of our first manuscript which we intend to submit by December 2015).
In all we are pleased to report that we are on schedule for a complete project report by February 2016 in time for the March review meeting. That said we are still very interested in sampling opportunities (particularly within the US) should they arise.

Concerns

Concern: We are ahead of schedule and have detected our target compounds in the field. Our only concern is access to US sites. It is more complicated and costly dealing with international individuals. An ideal set up would be that as several passive sampling projects have been funded, a US site of known contamination can be pre-approved for access and investigative teams can conduct parallel sampling efforts to improve methods and provide standardized comparisons.

Appendix B: Standard Operating Procedures (Tasks 2 and 3):

Objective 2: Assess the stability of target compounds within the sampler film for deployment timescales.

Procedure:

1.) Dissolve ~2g EVA into 100 ml Methylene chloride. This can be scaled up. 200-250 ml solutions are able to be used efficiently for coating in this container size, and can be made fresh without much waste.

2.) Produce a stock solution of TNT and RDX in acetone. The concentration should be such that the total munitions spike into the EVA/DCM solution is less than 10% total volume (~200-400ml DCM).

3.) Spike the EVA solution with the acetone solution such that the final concentration is 1 ug/ml TNT/RDX.

4.) Coat plates per usual SOP, dip the plates, let dry for a few moments, and repeat a total of 3 times. Final weight on the plate should be ~0.50-0.80 g EVA. Produce triplicates, and decide on time span. Make a set of 3x plates for each time point.

5.) The plates are then foil wrapped and individually bagged by time point, then placed into a 0˚C refrigerator.

6.) At the appropriate time scale, remove the plates, and extract using 2x 250-500ml Methanol soaks. Collect the methanol fraction, spike with 0.2 ug recovery standard (3,4-DNT), reduce by rotary evaporation to ~25ml, and then add 20ml Acetonitrile, and reduce further to ~5ml solution.

7.) Transfer to a Kuderna Danish concentrator vial. Reduce to 1 ml of Acetonitrile via a gentle stream of ultra high purity (UHP) Nitrogen gas (Airgas).

8.) Transfer the 1 ml of solution to an amber-glass GC vial.

9.) Samples were kept in cold storage (~0˚C) until two time points were collected. This was done to reduce instrument drift over time.

Objective 3: Optimize sampler geometries and film thicknesses for the detection of target field concentrations (below nanograms per liter).

Procedure 1: Thin film samplers (Rate kinetic)

1.) Dissolve ~2g EVA into 100 ml Methylene chloride. This can be scaled up. 200-250 ml solutions are able to be used efficiently for coating in this container size, and can be made fresh without much waste.
2.) Coat plates per usual SOP, dip the plates, let dry for a few moments, and repeat a total of 3 times. Final weight on the plate should be ~0.50-0.80 g EVA. Produce triplicates, and decide on exposure time.
3.) The plates are then exposed, collected, foil wrapped and individually bagged by time point, then placed into a -20˚C refrigerator (from our time-lapse study).
4.) Extract using 2x 250-500ml Methanol soaks. Collect the methanol fraction, spike with 0.2 ug recovery standard (3,4-DNT), reduce by rotary evaporation to ~25ml, and then add 20ml Acetonitrile, and reduce further to ~5ml solution.
5.) Transfer to a Kuderna Danish concentrator vial. Reduce to 1 ml of Acetonitrile via a gentle stream of ultra high purity (UHP) Nitrogen gas (Airgas).
6.) Transfer the 1 ml of solution to an amber-glass GC vial.
7.) Samples were kept in cold storage (~ - 4˚C) until analysis.

Procedure 2: Integrative Samplers (Larger Concentrations/Longer Exposures)

1.) Dissolve ~2g EVA into ~100ml Methylene Chloride in individual vials.
2.) Weigh the integrative sampler wells after they have been cleaned with acetone and dried.
3.) Using the integrative sampler wells, we gently warm the EVA/DCM solution (~30˚C) and then pour into the well quickly, to reduce air bubbles.
4.) The solvent is evaporated under gentle stream of Nitrogen until the coating is fully free of solvent. This can be tested by placing the plate on a balance and checking for reduction in weight over time.
5.) The plate is deployed, and exposed for the decided time scale.
6.) After collection, the polymer is removed from the well, and placed into a 50ml Eagle Tube (plastic centrifuge tube) and kept at -20˚C until extraction.
7.) Extract using 2x 250-500ml Methanol soaks. Collect the methanol fraction, spike with 0.2 ug recovery standard (3,4-DNT), reduce by rotary evaporation to ~25ml, and then add 20ml Acetonitrile, and reduce further to ~5ml solution.
8.) Transfer to a Kuderna Danish concentrator vial. Reduce to 1 ml of Acetonitrile via a gentle stream of ultra high purity (UHP) Nitrogen gas (Airgas).
9.) Transfer the 1 ml of solution to an amber-glass GC vial.

10) Samples were kept in cold storage (~ - 4˚C) until analysis.

Appendix C: Field Deployment Data

Station	Latitude	Longitude	Depth	Distance from UXO	Deployment time
Bedford Harbor Nova Scotia (August 2015)					
H0	44º42'22.10ºN	63º37'57.00ºW	2 m	Tidally flushed control no UXO	72 hours
H1	44º42'36.64ºN	63º38'41.57ºW	32m	RMC training site, distance to UXOs unknown (no ROV)	72 hours
H2	44º42'37.52ºN	63º38'33.22ºW	23m	RMC training site, distance to UXOs unknown (no ROV)	72 hours
Baltic Sea: (September 2015)					
B1	54º51'16.75ºN	19º10'22.36ºE	100m	Gdansk Deep, 20m from shipwreck	86 hours
B2	54º54'28.89ºN	19º21'13.06ºE	100m	Gdansk Deep, 2m from shipwreck	6 months

Appendix D through E:

Spreadsheets are all available in Dropbox

https://www.dropbox.com/sh/9fbd54w677ai8vq/AADCA11DBw37UJKEKzaQn2VQa?dl=0