FINAL REPORT

Multipurpose Sediment Passive Sampler with Improved Tissue Mimicry to Measure the Bioavailable Fraction

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14. ABSTRACT
There exists a need to develop low-cost passive samplers to monitor both metals and organics contamination in sediment in an integrative and quantitative manner. This was accomplished by the development of passive samplers prepared using a swellable organosilica material, Osorb media, to capture both dissolved organics, e.g., munitions, and metals, e.g., Pb(II), Cu(II), and Zn(II), from water and sediment. It was also demonstrated that the Osorb media can be loaded with triolein to mimic the tissues of benthic organisms without significant loss in capacity for the contaminants.

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passive sampler; sediment; explosives; environmental monitoring

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Table of Contents

Figures & Tables

List of Acronyms

A - area of the exposure surface
C_{free} - aqueous phase concentration
C_{irrev} - concentration irreversibly bound to soil particles, which is not available for bioaccumulation
C_{L} - concentration in lipid phase
C_{rev} - concentration reversibly bound to soil particles
C_{total} - total concentration of contaminants in sediment, including free, reversibly, and irreversibly bound species
C_{w} - concentration in the water phase
GCMS - gas chromatography mass spectrometry
EPA - Environmental Protection Agency
EqP - equilibrium partitioning theory
HOC - hydrophobic organic contaminant
k_0 - overall mass transfer coefficient
K_{Lw} - triolein-water partition coefficient
K_{mw} - membrane-water partition coefficient
K_{m} - membrane-lipid partition coefficient
k_{p} - mass transfer coefficients across the membrane boundary layers
k_{w} - mass transfer coefficient across the aqueous boundary layer
OSU-STAR - The Ohio State University Service Testing and Research Laboratory
PAH - polyaromatic hydrocarbon
PCB - polychlorinated biphenyl
PRC - performance reference compound
SPMD - semipermeable membrane device
SPME - solid-phase microextraction
TOC - trace organic compound
V_{L} - triolein volume

Keywords

passive sampler, sediment, explosives, chlorinated polyaromatics, environmental monitoring

Abstract

Objectives. The goal of the project was to utilize ABS Materials swellable organosilica media to build and evaluate a passive sampler design that would possess the following attributes:

- Be able to measure a wide range of analytes including high logK_{ow} species (dioxins and chlorobenzofurans) as well as more polar compounds (TNT and RDX) and metals (Cu, Zn, Ni, and Pb).
- Using the ability of the media to expand and contract, create sorbents which possess an adsorptive capacity that mimics benthic organisms to better inform remedial action decisions.
- Provide a design that has a significantly lower cost than current passive samplers.
- Create samplers which are easy to deploy and can be analyzed by major commercial testing labs using standard methods.

Technical Approach. The technical approach taken to address the objectives were as follows:

- Passive samplers were developed and tested using three different versions of Osorb® media to determine the optimal formulation for capture of metals, chlorinated polyaromatic compounds, TNT, and RDX.
- The fundamental performance of the passive samplers was tested in water to determine (A) time to equilibrium for analyte absorption, (B) sampler response to absorption of varying analyte concentrations as a measure of sensitivity, and (C) resistance to back diffusion to determine if response is integrative.
- The use of the passive samplers in sediment was analyzed using artificial sediment doped with varying concentrations of analytes. Recovery of sequestered chemicals within the Osorb passive samplers was completed to determine the % capture of both metals and munitions.

Results. The major findings of the project were the following:

- Three different versions of Osorb® media were synthesized and tested for adsorption of metals, chlorinated polyaromatic compounds, TNT, and RDX. The optimal media was able to measure chlorinated polyaromatics, munitions, and metals simultaneously with high capacity allowing the media to act as an infinite sink.
- Passive samplers using Osorb media demonstrate a fast response time (minutes-hours) due to the open mesh design. There is linear correlation between concentration in the environment and sampler response.

- The high capacity and affinity of the media acted as a sink allowing the measurement of analytes in both the pore water and those that are reversibly bound to sediment. As such, the sampler may be able to mimic the tissue of benthic organisms.

Benefits. The unique aspects of the sampler as designed and tested (i.e. low cost, fast capture rate, wide specificity) could open up new possibilities in sampling to provide data sets to site managers that are currently unavailable. Two examples are the following:

- Data indicate that Osorb media acts as an adsorptive sink for contaminants. If the partition coefficients of contaminants to the media indeed mimic fish tissue, the sampler could be used as direct measure of ecological impact. Such data could eliminate the need of costly bioassays.
- The fast uptake kinetics and proportional response to analyte concentration make the Sentinel™ passive sampler ideal for measurement of contaminants in stormwater. An array of passive samplers could be deployed at many stormwater collection points across an installation or throughout a near-shore watershed to provide a geospatial mapping of contaminants from a storm event. Monitoring inputs of pollutants is vital to understanding the sources of potential future sediment contamination. Knowledge of inputs could prevent costly measures such a re-dredging a site or undertaking additional unanticipated remediation measures.

Additionally, the successful completion of this project has resulted in the development and commercialization of the Sentinel™ passive sampler.

- The cost a single sampler is approximately \$25 (and less in bulk), which is cost efficient compared than other designs currently on the market.
- Post-deployment extraction and analysis can be done in a user's laboratory or the sampler can sent to Alloway Environmental Testing.
- Third party validation has been performed with the U.S. Navy, Oklahoma State, USGS, and U.S. Department of Energy. Some of these third party findings have already been published in the peer review literature.
- Patented media with technology transfer fully completed.

Benefits of Passive Samplers Developed in this Project	
Biomimic Sorbents High capacity combined with the ability to be in direct contact with sediment allows for sampler to mimic biological tissue. **Result:** Direct measurement of bioavailability.	**New Types of Sampling Regimes** Fast uptake allows both sediment and input water to be tested with the same device. Tracks sources of contamination. **Result:** Prevents future site remediation.
	

Objective

Summary. The objective of this work was to develop and test a multipurpose passive sampling system to measure the bioavailable fraction of chemicals of concern, including explosive residues, polychlorinated dibenzo dioxins, polychlorinated dibenzo furans, and metals. To accomplish this, thiolated organosilica sorbents with the trade name of Osorb® media, were used to mimic the metal ion binding proteins found in biological systems. Passive samplers were designed to have high capacity to rapidly assess the fraction of bioavailable compounds in sediment. This approach allows for a wide range of contaminants to be measured using a power-free, one-piece unit with a sorbent that closely resembles a biological matrix. Initial testing has shown that Osorb media has multi-analyte performance co-adsorbing chlorinated polyaromatics, explosives, and metals. Passive sampler technology for PCBs using polymer films has already been established. The unique aspects of Osorb media are the ability to equilibrate rapidly and capture explosives <u>and</u> metals. Review panel guidance stated that ABS Materials should focus on the sampling and detection of explosives and metals, as improved technology is needed to fill this gap in environmental monitoring.

At the onset of the project, passive samplers used swellable organosilica with triolein filled pores as the primary absorption matrix for organic analytes. Triolein has been used in semipermeable membrane devices for passive sampling due to its similarity with aquatic organism fatty tissues. Our approach uses a unique organosilica material that swells up to 8 times its dry mass in organic solvents. Commercially available as Osorb® media, swellable organically modified silica rapidly absorbs organic liquids upon contact expanding in volume. Initially, the hypotheses and objectives of the project were the following.

Key hypotheses to be tested:

(1) A triolein loaded Osorb matrix can serve as a high capacity sink to directly measure the bioavailable contaminant load via passive sampling.
(2) Mass transport limitations will be significantly reduced by creating a composite organosilica - triolein material that allows intimate contact between the lipid and the aquatic environment.
(3) Metals and organics can be measured concomitantly via incorporation of both hydrophobic liquid phase and metal ion binding sites, similar to those found in biological systems.

Technical Objectives:

(1) Prepare Osorb-triolein passive samplers and test binding affinity and capacity from aqueous solutions.
(2) Determine the ability of the Osorb-triolein passive samplers to measure the bioaccessible fraction of contaminants using spiked sediments.
(3) Confirm that both organics and metals are co-sampled with the mixed mode sampler.

Given the lack of passive samplers for more polar contaminants, the focus of this work was adjusted towards the detection of munitions and dissolved metals in sediment and seawater. Sediment was artificially contaminated with known amounts of TNT, RDX, Cu^{2+}, Pb^{2+}, Ni^{2+}, and

Zn^{2+} to study the effectiveness at capture of these species using the Osorb passive samplers. In addition, samplers were provided to the U.S. Navy (ER-201433, project leader: Gunther Rosen) for munitions detection in seawater.

Initially, Osorb media was loaded with triolein via the unique swelling mechanism of the organosilica sorbent to mimic the tissues of benthic organisms. Such work was completed and the adsorption affinity and capacity was tested. It was determined during the mid-year review that the addition of triolein into the passive sampler to study bioaccumulation will unnecessarily complicate the analysis of the samplers, and make these samplers less attractive from a user's ability to obtain data at reasonable cost and effort. Therefore, it was suggested by the technical panel to remove the triolein from the Osorb media within the passive samplers. This will enable ease of manufacturing and analysis, negating the need to do a separation step prior to detection.

The proposed work post modification of the project goals by the technical review committee was divided into six tasks to be accomplished throughout the tenure of the grant:

Task 1: Synthesize and characterize Osorb® media and prepare samplers
Task 2: Obtain and prepare sediment
Task 3: Characterize sediment to determine fractions
Task 4: Sampler testing
    4-1: Optimization of passive sampler composition for munitions and metals and preparation of new samplers
    4-2: Determine time to equilibrium for analyte adsorption
    4-3: Determine sampler response versus analyte concentration
    4-4: Determine resistance to desorption to verify integrative response
Task 5: Use of passive samplers in sediment
Task 6: Conclusions and documentation

Background and Significance

Environmental monitoring and remediation action strategies require accurate measurements of the impact contaminants of concern on terrestrial and aquatic organisms. Discrete sampling of water and sediment followed by laboratory analysis is a standard practice. Total concentration data provided by discrete measurements provides a baseline understanding of contaminant distribution, but provides only limited information on toxicity potential since a total concentration value may not predict to what extent pollutants are accessible to organisms. Passive samplers provide an alternative option to discrete sampling.[1-3] Typically passive samplers have targeted the collection of trace organic compounds (TOCs), such as polychlorinated biphenyls (PCBs)[4-10] and other non-polar analytes such as polyaromatic hydrocarbons (PAHs)[11-13], and other micropollutants.[14] The integrative nature of passive samplers is useful in obtaining time weighted averages in water streams and increasing concentrations above method detection limits by accumulation over time. Passive samplers have been applied to the measurement of TOCs in sediment, especially PCBs. Special emphasis has been placed on mimicking the uptake of PAHs and PCBs by benthic organisms in order to illuminate the potential for adverse impacts on aquatic ecosystems without having to use live organisms and tissue extractions.[5] As such, significant research has been accomplished developing biomimetic models,[15,16] equilibrium models,[17,18] and devices to simulate bioaccumulation.[19-20]

It is important to understand where contaminants are found in sediments, how source location affects bioavailability, and why passive sample design is critical. Schwarzenbach et al. have stated that the key in understanding the risk of hydrophobic organic contaminants (HOCs) in aquatic environments is measuring bioavailability.[25] Reichenberg and Mayer have proposed that there are two parameters governing bioavailability: bioaccessibility and chemical activity.[26] These are derived from the fact that contaminants, with respect to aquatic organism exposure, are either: (*i*) irreversibly bound to sediment; *(ii*) reversibly bound, or (*iii*) freely dissolved (Figure 1). The reversibly bound pool and freely dissolved pool are both bioaccessible whereas irreversibly bound is not. Important notes: Traditional sediment extraction methods, such as Soxhlet extraction measure C_{total}, which will overestimate the biotoxicity to aquatic organisms if the irreversibly bound fraction is significant. Equilibrium based passive sampling using low capacity polymer films is employed to assess the bioavailable fraction by measuring the chemical activity[27] – i.e. the contributions of partition of contaminants reversibly bound to sediment sites and that in the freely dissolved phase. Due to the limited capacity and the non-polar character of the analytes, such as PAHs and PCBs, the amount of hydrophobic organic chemicals captured is dominated by those partitioning from C_{free}. Literature shows that passive samplers of these designs are effective in measuring C_{free}.[28] Equilibrium partitioning theory (EqP), in various forms, is then used to attempt to estimate the bioavailability from C_{free}. However, use of EqP may introduce considerable inaccuracy and that the environmental risks may be drastically overstated. For instance, contribution of black carbon and soot in natural sediments act as strong sinks of contaminants and are not adequately accounted for by EqP and may lead to significant overestimation of toxicity.[29]

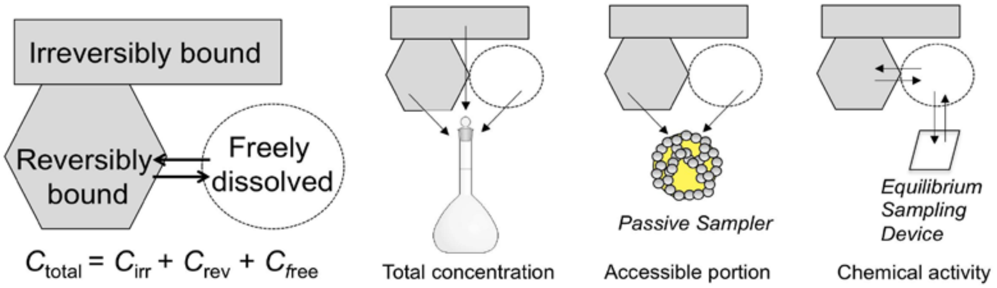


Figure 1: Contaminants in sediments are located in pools relative to their bioavailability including fractions irreversibly bound to sediment particles, fractions reversibly bound to sediments, and compounds found in the freely dissolved state that are in equilibrium with the reversibly bound fraction. The total concentration is the sum of the three pools. Traditional sediment analysis uses extensive extraction methods and measures C_{total}. Low capacity passive samplers come to equilibrium with the C_{free} and measure the chemical activity of a contaminant. High capacity Osorb based passive samplers are proposed to directly sample the accessible potion.

There is scientific debate over whether C_{free} can be used to assess bioavailability. Reliance of measurements of chemical activity result from passive sampler designs that have, to date, been fabricated from "off the shelf" materials such as polyethylene, polytetrafluoroethylene, or cellulose. Our approach is to use advanced materials to create a passive sampler system that can measure *both* the freely dissolved and the rapidly desorbing fraction (Figure 1). Moreover these materials will be designed to better mimic aquatic organism tissues and target adsorption of *both* metals and organic compounds. The concept mirrors the use of porous polymer materials such as Tenax[30], HP-20[31], or silicone[32] to create passive samplers where the capacity of the sorbent is designed to be dominating. Bioaccessibility is thus directly measured by fully depleting both the reversibly bound fraction (C_{rev}) and freely dissolved pools (C_{free}) as would occur on an organismal level.[33] Simultaneous measurement of both $C_{f\mathrm{ree}}$ and C_{rev} will allow for measurement of bioaccessibility without significant use of modeling. Within a regulatory context, this will allow decisions to made on the extent of accessible contaminant loads instead of C_{total}. Since C_{total} may drastically overestimate environmental impact, such data will allow improved decision making capabilities. Specifically, we will use a high swelling organosilica continuously porous solid filled with triolein to act as a biomimic, high capacity passive sampler.

The work proposed here is focused on a significant improvement on the design of sediment passive sampling devices by using recently discovered swellable organosilica matrixes.[21] Previous sediment passive samplers have involved semipermeable membrane devices (SPMDs) where a solution or film of the triglyceride triolein, to simulate fish lipid, is contained in a low density polyethylene tube or pouch-like container[22] Small non-polar organic contaminants are supposed to partition into the membrane, diffuse through the polyethylene, and then partition into the triolein. Multi-term mathematical expression was developed by Huckins[23] to describe the exchange of contaminants between the water and a SPMD of the polyethylene-triolein design.

Description of Osorb media. Mesoporous organosilica materials created for analytical detection of trace explosive residues led to the development of the technologically advanced Osorb® silica-based sorbents manufactured by ABS Materials, Inc. Hydrophobic porous organosilicas were pioneered by Cerveau & Corriu and Loy & Shea[34] using sol-gel polymerization processes where the characteristics are tailored by controlling the kinetics of hydrolysis and condensation reactions of alkoxysilanes.[35-37] Our patented media builds upon the material science of organosilica materials by using specialized organically bridged precursors that can participate in molecular self-assembly during sol-gel polymerization. An example of a structure directing precursor is bis(trimethoxysilylethyl)benzene (BTEB) which has an aryl ring flexibility linked to two silicon centers.[42] Using acid or base catalysis, the Si-OCH_3 groups undergo hydrolysis and condensation to create a Si-O-Si linked polymer. Molecular-to-microscale organization is directed by π-π stacking interactions between the aryl groups.[41] As a result, the three dimensional matrix becomes ordered as measured by optical birefringence and powder x-ray diffraction.[43-45] The final microscale architecture consists of a network of ~20 nm particles interlinked into a highly porous network which is ideal for extracting molecules from soil and water.[47] Organization and micro-phase separation during the polymerization process orients the phenylene groups on the surface of the porous organosilica, resulting in enhanced hydrophobicity and demonstrated ability to bind organic compounds such as trinitrotoluene[39,46], DDT[46], polyaromatic hydrocarbons[39], and similar compounds.[48]

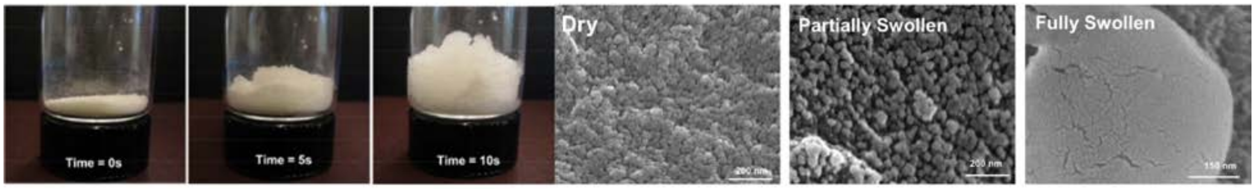


Figure 2: Left: Osorb expansion upon drop-wise addition of acetone. Right: Electron micrographs of: Dry, Partially swollen, and Fully Swollen: Osorb in ethanol followed by critical point drying showing the fully expanded state. (scale bars: 200 nm).

Experimenting with the processing conditions led to the discovery of a special type of porous architecture that results in a flexible matrix capable of expanding 3-4 times in volume upon absorption of organic liquids.[49] Flexibility in the organosilica matrix is created by careful control over the kinetics of interparticle crosslinking via choice of catalyst, solvent, and molecular-scale self-assembly. Technically described as swellable organically modified silica (SOMS), these materials demonstrate very high capacity to bind both neat and dissolved phase organic molecules. Absorption is facilitated by the linking of nanoscale organosilica particles into a macroscopically hard, yet animated, array (Figure 2). The remarkable absorption capabilities of SOMS for volatile organic compounds[54] and pesticides has led to the commercialization of the material as Osorb media by ABS Materials. Osorb media is used for water treatment including stormwater and produced water,[50,51] in addition for use in passive sampling.

Metal ion binding sites were added to the surface of the organosilica by co-polymerization of amine and thiol containing alkoxysilane precursors with the primary matrix formation precursors. Preliminary work has shown that a 10% mol:mol addition of mercaptopropyl groups leads to a 3 mg/g binding capacity of the Osorb matrix with little impact on swelling. Thus, using a thiolated Osorb media will allow for concomitant measurement of both organics and metals. Thiol groups of proteins are the primary binding sites of toxic metals in the cell leading to a host of non-specific effects. Thus, the chemical interactions built into the Osorb matrix would be designed to mimic a biologic system without the need to use proteins. Overall, the Osorb particle loaded with triolein will possess two distinctly different modes of binding contaminants: (i) hydrophobic organics via partitioning into the triolein liquid phase and (ii) strong metal ion binding via thiol groups located on the inside and outside surfaces of the media (Figure 3). [*Note:* Triolein loaded Osorb particles were created and the adsorption tested. Although the loaded particles successfully adsorbed target compounds, midway through the project timeline we reverted to using Osorb media without triolein. Using media was suggested by the review panel since the system is simpler and bare media was also successful in adsorbing target compounds.]

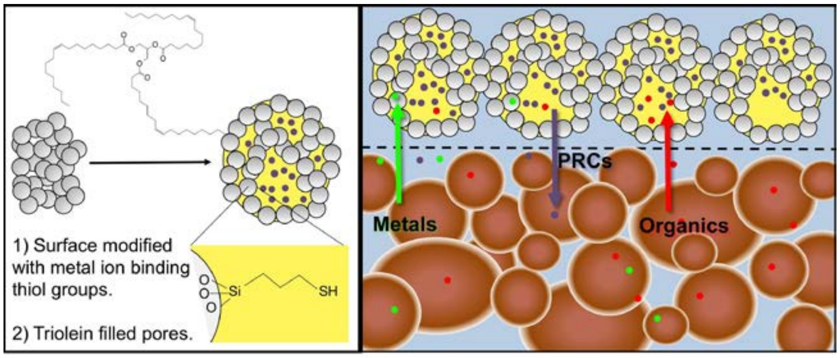


Figure 3: Concept of Osorb based passive samplers. Osorb media, a flexible array of organosilica particles, will be synthesized using established protocols to swell and possess 10% mol:mol of silane precursors with a thiol containing pendant group. The swelling will be used to fill the matrix with triolein loaded with a performance reference compound (PRC). The particles will be added into a mesh housing at the end of the sampler and will measure the accessible organics (red) and metals (green). [*Note:* Although successfully created and tested, the triolein loaded design was discontinued during the project to use bare Osorb media particles as the sorbent phase.]

Materials and Methods

Materials. Standards of contaminants were obtained from Sigma-Aldrich and Restek. Silica sand was obtained from US Silica, while kaolin silt and clay were obtained from BASF.

Sorbent synthesis. Osorb media is made via a proprietary sol-gel method by ABS Materials, Inc.[52] Initial performance data was collected using three different organosilica medias that were prepared and characterized for use as the swellable media in the passive samplers: Osorb_A media was a modified silica composite matrix, Osorb_B media was a functionalized matrix, and Osorb_C media was a metal oxide organosilica composite. Osorb media was ground and sieved to a 35-60 mesh particle size (250-500 μm) for testing.

Sampler construction. Media (500 mg) was placed in 150 mesh stainless steel which was closed with a grommet. The dimensions were 6.5 cm in length and 1.5 cm in width.

Capture from simulated seawater and aqueous solutions. Sampling containers were filled with 3.5 L of chlorine free tap water and simulated sea water. Simulated seawater was prepared following an adapted literature protocol using the commercial product, Instant Ocean®.[53] The water was spiked with Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, RDX, and TNT at varying concentrations: 0.2, 0.8, 1.9, 7.6, 50 ppb. Samplers were added to each of the water samples, which were left stirring to simulate a fluid water sample, for 48 hr. It was determined in work conducted that 24 hr is sufficient to reach equilibrium, thus ensuring equilibrium at 48 hr. All testing was done in triplicate.

Sediment preparation. After a careful review of the literature, an EPA method was identified that combined silica sand, kaolin clay, and kaolin silt to prepare artificial sediment.[54,55] Batches of the sediment were prepared by adding 80% silica sand (F-65), 15% kaolin silt (ASP400P), and 5% kaolin clay (ASP900) by weight into a cement mixer. The sediment was mixed for 1.5 hr to ensure homogeneity. This resulted in very fine sediment; the particle size of the different components was in the micron size range (Task 2.1, Table 8, below).

Elution. Organics were eluted with 15 mL of dichloromethane with 1% acetic acid (to prevent deprotonation of TNT). The solvent was evaporated by dry air flow and residues reconstituted in acetonitrile for HPLC or dichloromethane for GC-MS. Following desorption of organics the passive sampler was dried and the media removed and placed into an empty solid phase extraction cartridge. Metals were desorbed using 2 x 2 mL aliquots of 6M HCl.

Analytical methods. RDX and TNT was measured using HPLC with UV detection (Agilent 1100 HPLC with diode array detector). A C18 column (Agilent) was used with a mobile phase of acetonitrile and water with 0.1% phosphoric acid. Gradient elution was used starting at 35% acetonitrile ramping to 100% acetonitrile over 15 min. In some cases HPLC with mass spectrometry was used to confirm results using a Agilent 1200 HPLC with Series 6400 MS/MS Triple Quadrupole.[56] Gas chromatography was used to measure the concentration of chlorinated species and TNT using an Agilent 6890/5973 GC-MS, ChemStation and NIST98 MS database.

Results and Discussion

Task 1: Synthesize and Characterize Osorb® Media and Prepare Samplers

(1-1) Synthesis of Metals Capture Osorb Media. Prior to the passive sampling devices being developed, preliminary testing was completed to design the most effective organosilica media for the capture of both dissolved organic species, e.g., TNT, RDX, and dissolved metal ions, e.g., Zn^{2+} and Pb^{2+}. The base material used for the development of these advanced organosilica medias was Osorb media, which is a flexible organosilica that has the unique ability to "catch and release" organic species. This "catch and release" mechanism allows for the capture of dissolved species in water via a partition equilibrium mechanism, and then later enables the release of these contaminants from the media via flushing the sorbent with an organic solvent. The Osorb media will swell upon exposure to neat organic compounds, which effectively flushes the contaminants out of the sorbent for analysis via standard analytical methods, e.g., GCMS or LCMS. Osorb media is made via a proprietary sol-gel method by ABS Materials, Inc. in Wooster, OH.

Initial performance data was collected using three different organosilica medias that were prepared and characterized for use as the swellable media in the passive samplers: Osorb_A media was a modified silica composite matrix, Osorb_B media was a functionalized matrix, and Osorb_C media was a metal oxide organosilica composite (Figure 4). The Osorb medias were synthesized according to proprietary methods and ground and sieved to a 35-60 mesh particle size (250-500 μm) for testing.

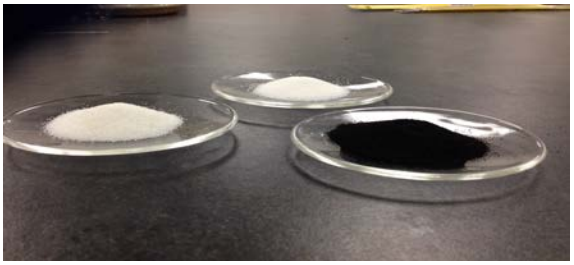


Figure 4. Three different Osorb medias were synthesized to be tested for metals and organics capture for the use in passive samplers.

Osorb media were evaluated for organic (Table 1) and metal (Table 2) capture using standard in-house testing methods. Capacity and efficiency for dissolved toluene is a standard QC column test method for Osorb media; all three medias performed similarly when normalized for Osorb media content, demonstrating a dissolved toluene capacity of 0.33-0.34 g/g and >99% efficiency. The capture of neat solvent and triolein varied between the three Osorb medias. It is proposed this is due to a difference in pore structure. The medias were evaluated for metals capture via batch equilibrium testing. The water samples before and after exposure to 1% w/v Osorb media were analyzed using a Prodigy Dual View Inductively Coupled Plasma Spectrophotometer using a nitric acid microwave digestion assay. Capture of Cu^{2+}, Zn^{2+}, and Pb^{2+} were individually and collectively tested. All Pb^{2+} samples and a majority of the Cu^{2+} were below the detection limit of the instrument after exposure to the Osorb media. No significant difference was observed in removal efficiency of dissolved metals between the three different Osorb medias.

The second phase of testing of the media focused on unmodified Osorb media, which has been studied extensively by ABS Materials for capture of a wide range of organic contaminants. This media was included in the testing plan to specifically target munitions, e.g., RDX, TNT. This media is currently used for passive sampling applications in the ABS' commercial product, "SENTINEL™ Passive Sampler". The second media synthesized was the thiol (-SH) functionalized media ("Osorb_A media") for the capture of dissolved metals, which has demonstrated to have a high affinity for dissolved metals, while having chemistry that can desorb the metal ions for analysis. It was hypothesized that although the thiolated version of the media also had the ability to adsorb organic molecules, in addition to dissolved metals, there would be improved capture for the munitions with some percentage of standard Osorb media present in the sampler composition.

Table 1. Initial testing results for organics capture for the three organosilica Osorb media versions.

Media Sample	**Volumetric Swell in Acetone**	**Acetone absorption (mL/g, g/g)***	**Triolein absorption (mL/g, g/g)***	**Dissolved Toluene Capacity (g/g)#**	**Dissolved Toluene Efficiency**
Osorb_A	410%	7.8, 6.2	3.8, 3.6	0.34	>99%
Osorb_B	220%	3.3, 2.6	1.7, 1.5	0.33	>99%
Osorb_C[╜]	240%	7.8, 6.2	3.1, 2.8	>0.34	>99%

* gram chemical specie per gram of Osorb media, as synthesized, [#] normalized for Osorb media content

Table 2. Capture of dissolved metals using various Osorb medias. (Top) Capture of Cu^{2+}, Zn^{2+}, and Pb^{2+} in individual samples; (bottom) capture of dissolved metals from a mixture of the three in water. Metal concentrations were analyzed using a Prodigy Dual View Inductively Coupled Plasma Spectrophotometer using a nitric acid microwave digestion assay with detection limits of 2.16 ppb, 1.56 ppb, and 4.32 ppb for Cu^{2+}, Zn^{2+}, and Pb^{2+}, respectively. Raw data can be found in Appendix A, Table 1.

Osorb Media Sample	**Capture of Cu^{2+}**			**Capture of Zn^{2+}**			**Capture of Pb^{2+}**		
	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal
_A	40.4 ± 0.3	4.0 ± 2.8	90.2 ± 6.9	44.2 ± 0.7	10.8 ± 1.5	75.4 ± 3.8	27.3 ± 0.3	4.0 ± 0.0	85.4 ± 0.2
_B	40.4 ± 0.3	2.0 ± 0.0	95.0 ± 0.0[γ]	44.2 ± 0.7	12.7 ± 3.1	71.2 ± 7.5	27.3 ± 0.3	4.0 ± 0.0	85.4 ± 0.2
_C	40.4 ± 0.3	2.7 ± 0.7	93.2 ± 1.8	44.2 ± 0.7	11.7 ± 0.8	73.4 ± 1.4	27.3 ± 0.3	4.0 ± 0.0	85.4 ± 0.2

Osorb Media Sample	**Capture of Cu^{2+}**			**Capture of Zn^{2+}**			**Capture of Pb^{2+}**		
	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal	Initial Conc. (ppm)	Post Exposure to Osorb Media (ppm)	% Removal
_A	40.6 ± 1.3	2.2 ± 0.3	94.6 ± 0.6[γ]	46.4 ± 1.4	12.3 ± 2.1	73.5 ± 1.4	30.9 ± 1.2	4.0 ± 0.0	87.0 ± 0.2[γ]
_B	40.6 ± 1.3	2.0 ± 0.0	95.1 ± 0.1[γ]	46.4 ± 1.4	10.7 ± 2.9	76.8 ± 3.0	30.9 ± 1.2	4.0 ± 0.0	87.0 ± 0.2[γ]
_C	40.6 ± 1.3	3.5 ± 0.8	91.3 ± 1.4	46.4 ± 1.4	11.0 ± 1.0	76.4 ± 1.6	30.9 ± 1.2	4.0 ± 0.0	87.0 ± 0.2[γ]

[γ] Samples were below the limit of detection of the instrument.

Both medias were sieved to size (35-60 mesh) for testing purposes. The medias were physically blended to the following weight ratios (Standard Osorb media : Thiolated Osorb media): 100:0, 75:25, 50:50, 25:75, 0:100. Following blending, equilibrium batch testing was completed using the different Osorb formulations to specifically target munitions and metals; this was completed with bulk media, rather than the samplers, to correlate to data previously acquired (Table 3). The blended Osorb media (1% w/v) was used to capture a mixture of TNT, RDX, Cu^{2+}, Zn^{2+}, and Pb^{2+}. Initial concentrations were 50 ppb, 50 ppb, 180 ppb, 60 ppb, and 15 ppb, for TNT, RDX, copper, zinc, and lead, respectively. Equilibrium time was 1 min. Percent capture of each component by the Osorb media was analyzed using standard analytical methods (TNT and RDX: HPLC-UV; Metals: ICP-AE). Percent capture of munitions was determined based on HPLC-UV peak area differences. Percent capture of dissolved metals was determined by the concentration changes in the samples exposed versus unexposed to Osorb media, as analyzed via ICP-AES.

TNT is absorbed more strongly than RDX, with an average capture of 85% as measured via HPLC-UV peak area changes between triplicate samples of samples exposed to 1% w/v Osorb media compared to control samples. On average, there was a 61% capture of RDX. The type of media used had no effect, within error, on the percent capture in munitions.

Table 3. Percent capture of a mixture of munitions and dissolved metals using different ratios of Osorb media to thiolated media to determine the optimal formulation for the removal of both suites of contaminants of interest. It was determined to proceed with a ratio of 25:75 Osorb media : thiolated media, as indicated by the green highlighting, as a balance of performance, ease of manufacturing, and cost. Error reported is the propagated standard deviation between triplicate samples exposed to Osorb media relative to triplicate control samples. Raw data can be found in Appendix A, Table 2.

Osorb media+ Thiolated media	**% RDX Capture**	**% TNT Capture**	**% Cu^{2+} Capture***	**% Zn^{2+} Capture***	**% Pb^{2+} Capture***
0:100	64.1 ± 4.4	89.1 ± 19.1	82.9 ± 30.8	91.5 ± 20.1	73.3 ± 4.9[γ]
25:75	63.9 ± 9.4	87.1 ± 2.7	92.0 ± 20.4	72.9 ± 15.6	73.3 ± 4.9[γ]
50:50	59.4 ± 6.0	83.9 ± 16.0	93.1 ± 36.7	84.0 ± 17.0	73.3 ± 4.9[γ]
75:25	56.8 ± 1.5	79.2 ± 13.1	83.5 ± 74.3	66.0 ± 8.1	73.3 ± 4.9[γ]
100:0	59.4 ± 3.2	87.5 ± 8.4	53.0 ± 14.8	68.6 ± 12.5	42.2 ± 15.2

* Limit of detection of metals: Cu^{2+} 2.16 ppb, Zn^{2+} 1.56 ppb, Pb^{2+} 4.32 ppb.

[γ] Samples were below the limit of detection of the instrument.

Batch equilibrium binding results also indicate that the media effectively captures dissolved copper, zinc, and lead from solution. It is interesting to note that even standard Osorb media, which is not designed to covalently bond with dissolved metals, does adsorb a significant percentage of the dissolved metals at the parts-per-billion concentration range from solution, presumably due to the high surface area of the media. Introduction of a percentage of thiolated Osorb media does in fact improve the capture of dissolved metals from solution, as a significant increase in copper, particularly, was observed. Similar capture of copper, zinc, and lead was observed for media ratios of 75:25 50:50. 25:75 and 0:100 standard Osorb media : thiolated Osorb media, which indicates that the binding sites are likely not saturated.

(1-2) Loading of Osorb Media with Triolein as the Biomimicry Agent. The final passive sampler was not made using triolein as a biomimicry agent upon request from the technical panel due to complexity and cost of analysis, but initial work demonstrates the use of triolein and the effect of its presence on the performance of the organosilica sorbent for removal of dissolved organics from water. Triolein was chosen as a lipid surrogate for fish tissue to act as a sink for contaminants to simulate bioaccumulation. The triolein is a viscous triglyceride that can be loaded into the pores of the Osorb matrix at high levels, 1.5-3.6 g triolein per g Osorb media. Once the Osorb medias were fully loaded with triolein, the biomimic Osorb media was loaded into a column to test the dissolved toluene capacity following the standard QC method after being fully loaded with the triglyceride. A column fraction from each column after 30 min was analyzed via IR spectroscopy to determine if triolein was desorbing from the media into the water. Infrared spectrometry indicted high retention of triolein within the Osorb matrix (Table 4). A slight increase in desorption of the triolein out of the Osorb_C matrix was observed in comparison to the other two medias.

Table 4. Retention of triolein in the Osorb media matrices after 30 min column at 1 mL / min flow rate.

Media Sample	**Amount of Triolein Retained**
Osorb_A	99.6%
Osorb_B	99.6%
Osorb_C	95.6%

To understand the differences in the absorption and desorption of organics between the three Osorb medias, a pore structure analysis was completed using BET nitrogen adsorption (Table 5). As hypothesized based on the triolein capacity and desorption, a difference in pore structure was observed for the three samples. Osorb_A media has a high pore volume (0.53 mL/g) with a high surface area (420 m^2/g) with the majority of pores <8 nm in diameter. Similarly, Osorb_B media has small pores, <6 nm, with a smaller pore volume (0.34 mL/g), which indicates additional cross-linking of the matrix. This possibly explains the lower capacity for triolein; the tighter matrix may inhibit diffusion of the large triolein molecules into the interior of the pore structure. Most interestingly, Osorb_C media demonstrates a significantly different pore structure compared to the other two medias. The presence of larger metal oxide particles may lead to the nanostructure assembly process being altered, resulting in larger pore diameters. The larger pore sizes may lead to improved diffusion in and out of the matrix of the media. Scanning electron microscopy analysis visually shows the difference in pore structure (Figure 5).

Table 5. BET pore volume analysis of the three Osorb medias. The surface area and pore volume of Osorb_C media was normalized for Osorb media content.

			Pore Size Distribution							
Osorb Type	Surface Area (m^2/g)	Pore Volume (mL/g)	<6 nm	6-8 nm	8-10 nm	10-12 nm	12-16 nm	16-20 nm	20-80 nm	>80 nm
A	420	0.53	63.3	26.8	3.5	2.1	1.7	0.8	1.5	0.3
B	310	0.34	92.6	2.7	1.3	0.9	0.7	0.5	1.1	0.3
C*	490	0.75	35	18	9.7	6.3	5.1	3.9	18.6	3.3

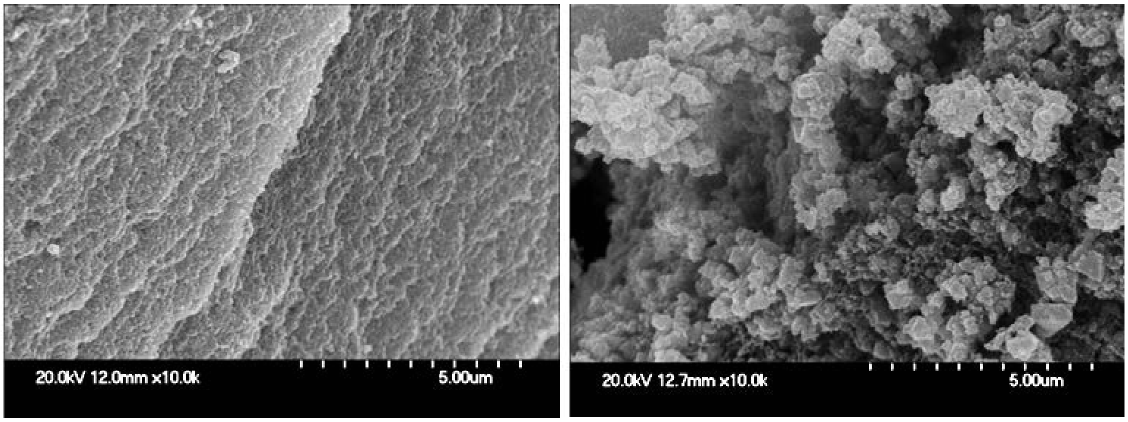


Figure 5. Scanning electron microscope images of an organosilica similar in structure to that of Osorb_A, B medias (left) compared to Osorb_C media (right); larger pores are observed in Osorb_C media.

After confirming that the majority of the triolein does not desorb out of the Osorb matrix over time, batch equilibrium testing for anthracene was done with 1% w/v Osorb media, as synthesized and preloaded with the triolein to compare capture efficiency after loading with the biomimicry agent (Table 6). Three different anthracene concentrations were tested: 175, 26.3, and 1.8 ppm. Percent capture of anthracene upon exposure to Osorb media or Osorb media loaded with triolein was done in triplicate and reported as an average concentration of anthracene post exposure to Osorb media (Table 6). A minor decrease in capture was observed for the Osorb media loaded with triolein, but the percent capture was still high (>95%). No significant differences were observed between the different types of Osorb materials.

Table 6. Batch equilibrium data for anthracene capture: Osorb media as synthesized compared to material preloaded with triolein. Aqueous solutions of anthracene at three concentrations were exposed to 1% w/v Osorb media or Osorb media preloaded with triolein. The concentration of anthracene in the water samples was quantified using GC-MS spectrometry and was reported in ppm and % capture.

Average Initial Concentration (ppm)	175.0 ± 5.1		26.3 ± 0.7		1.8 ± 0.2	
Osorb media as synthesized						
Osorb Media Sample	Average Anthracene Concentration Post Exposure to Osorb Media (ppm)	% Captured	Average Anthracene Concentration Post Exposure to Osorb Media (ppm)	% Captured	Average Anthracene Concentration Post Exposure to Osorb Media (ppm)	% Captured
_A	0.1 ± 0.1	99.9	0.0 ± 0.0	100.0	0.0 ± 0.0	100.0
_B	0.0 ± 0.0	100.0	0.2 ± 0.3	99.2	0.0 ± 0.0	100.0
_C	0.0 ± 0.0	100.0	0.0 ± 0.0	100.0	0.0 ± 0.0	100.0
Osorb media preloaded with triolein						
_A	6.0 ± 1.4	99.6	0.6 ± 0.2	97.7	0.1 ± 0.1	93.0
_B	7.3 ± 4.4	95.8	1.1 ± 0.7	95.9	0.1 ± 0.1	96.4
_C	8.8 ± 5.9	95.0	1.3 ± 0.5	94.9	0.0 ± 0.1	97.9

(1-3) Desorption of Performance Reference Compounds. The initial design for the development of biomimetic passive samplers stated that the samplers would be loaded with Osorb media preloaded with triolein as the biomimicry agent and performance reference compounds (PRCs) to enable a method of quantification based on the rate of back diffusion of the PRCs out of the matrix. It was later decided by the technical panel not to proceed with the use of PRCs due to the cost of the required deuterated or isotopically labeled PRCs. The initial testing is included here to demonstrate the validity of the concept. Initial testing was done using unlabeled anthracene as a surrogate for a PRC for cost reasons. Each of the three initial Osorb samples were fully loaded with triolein and a PRC (PRC dissolved into triolein at 0.5% w/w). The samples were retested for dissolved toluene capture, as it is the standard QC method of analysis for Osorb functionality. This was done to confirm no loss of capacity when fully swelled with the triolein. There was minimal loss in capacity for dissolved toluene after the media is loaded with the biomimicry agent (Table 7). The loading of the Osorb media with triolein does not significantly affect the ability of the Osorb media to capture contaminants out of sediment and/or water.

Table 7. Dissolved toluene column testing for the three different Osorb medias before and after loading.

	Prior to Triolein Loading		**Post Triolein Loading**	
Osorb Media Sample	Dissolved Toluene Capacity (g/g)	Dissolved Toluene Capture Efficiency	Dissolved Toluene Capacity (g/g)	Dissolved Toluene Capture Efficiency
Osorb_A	0.34	>99%	0.34	99.9%
Osorb_B	0.33	>99%	0.25	98.0%
Osorb_C*	>0.34	>99%	>0.34	98.8%

*normalized for Osorb media content

The back-diffusion of the PRCs out of the Osorb matrices was monitored over time simultaneously to the toluene capture (Figure 6). The back diffusion of the anthracene PRC out of Osorb_A is significantly different than that out of Osorb_C media. The mesoporous structure of Osorb_C media results in a greater diffusion of the PRCs out of the Osorb matrix. From this data, it is predicted that Osorb_A media could monitor 3448 L of water before the PRC was fully desorbed, while Osorb_C media could monitor 99 L of water. If there was a constant flow of water, the samplers made with Osorb_A media would last for 2396 days and those made with Osorb_C media would last for 69 days before complete diffusion of the anthracene PRC. This would be further enhanced in sediment, as it would not be a steady flow of water. Due to the long lifetime of the samplers, testing until full desorption of the PRC was not completed.

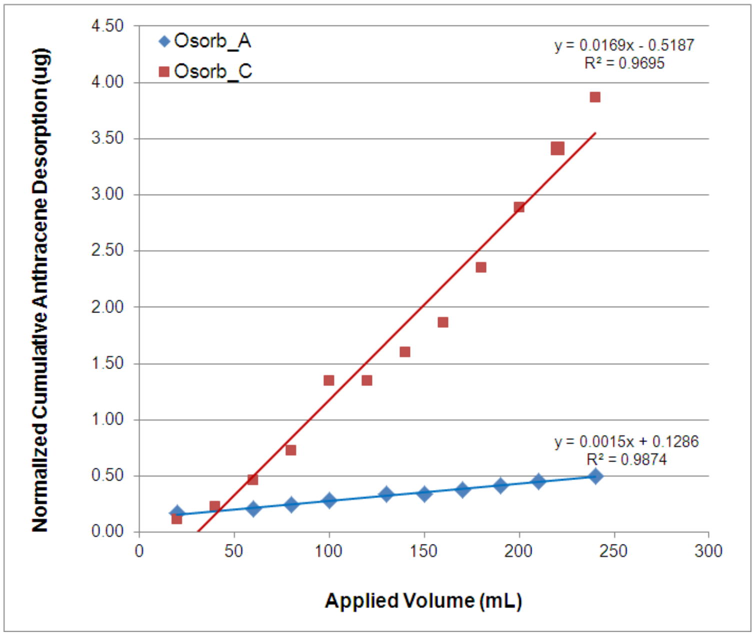


Figure 6. The normalized diffusion of anthracene, a surrogate PRC, out of triolein loaded Osorb media. The rate of diffusion of the anthracene varied depending on the type of Osorb media, presumably due to the differences in pore structure.

(1-4) Preparation of Samplers**.** Based on the results from the initial evaluation of the Osorb media performance, it was proposed that either Osorb_A or Osorb_C medias could be used for sediment monitoring, as they both could be loaded with high levels of triolein (when normalized for Osorb content) and they demonstrated high capacity for organics and metals. The small pore size of Osorb_B media limited the amount of triolein, and thus the PRC, that could be loaded within the Osorb matrix. Thus, this material has been excluded from further testing. Due to the enhanced performance and ability to effectively recover both metals and organics from the samplers for analysis, Osorb_A media was chosen as the sorbent for use in the samplers. The second phase of media evaluation post technical review resulted in a blend of standard Osorb media (for the capture of munitions) and the thiolated Osorb media (Osorb_A media) (for the capture of metal ions). Samplers were prepared using a weight blend of 25% standard Osorb media and 75% thiolated Osorb media, as capture was similar for the different formulations of Osorb media to thiolated media, as found in Table 3. Therefore, a 25:75 blend Osorb media to thiolated media was chosen as the inclusion of thiolated media did show to enhance capture of metal ions compared to the non-thiolated media. The thiolated media does require some modifications to the manufacturing process ABS Materials currently has, and therefore, inclusion of 25% Osorb media was maintained as a balance between cost, ease of manufacturing, and performance of media. The samplers were fabricated using stainless steel mesh and 500 mg of the identified media blend.

A manufacturing space and process was established for Osorb enhanced sampling devices. The first generation product is known as the Sentinel™ passive water sampler. A sampler for sediment monitoring for the detection of both munitions and dissolved metals was the goal of this SERDP funded project. A large number of samplers for testing (55+ samplers) were fabricated in stainless steel mesh (150 mesh) to accomplish the final phases of this project using the 25:75 weight blend of Osorb media:thiolated Osorb media (Figure 7).

Figure 7: Sentinel passive sampler design.

Task 2: Obtain and Prepare Sediment

(2-1) Obtain and Prepare Sediment. It was decided to evaluate the effectiveness of the passive samplers using a controlled sediment that was artificially prepared to minimize variabilities in the experimental setup. By producing a large quantity of artificial sediment, the carbon content, organic matter, and particle size was well controlled. This enables the samplers to be tested with homogeneous sediment samples that had been fully characterized for carbon and metal content prior to addition of a set amount of known contaminants.

After a careful review of the literature, an EPA method was identified that combined silica sand, kaolin clay, and kaolin silt. Batches of the sediment were prepared by adding 80% silica sand (F-65), 15% kaolin silt (ASP400P), and 5% kaolin clay (ASP900) by weight into a cement mixer The sediment was mixed for 1.5 hr to ensure homogeneity. This resulted in a very fine sediment; the particle size of the different components was in the micron size range (Table 8).

Table 8. The compositional of artificial sediment.

Sediment Components	Weight Percent	Manufacturer	Particle Size (µm)
silica sand	80%	US Silica	106-212
kaolin silt	15%	BASF	3.5
kaolin clay	5%	BASF	1.5

To understand the effect of the carbon content on the bioavailable fraction of contaminants within sediment, the artificial sediment was dosed with activated carbon (DARCO, 150 µm) at a concentration not to exceed 2% by weight (Figure 8). The carbon was added to the sediment components prior to mixation.

(2-2) Evaluation of Sediment. The artificial sediment samples were analyzed for carbon and nitrogen content using an Elementar America's VarioMax Carbon-Nitrogen Combustion Analyzer (Table 9). The nitrogen content was minimal. The carbon content varied from no detection for the base sediment to 0.18, 0.32, 0.65, 0.96, and 1.2% carbon (g/g) for the range of carbon loaded sediment samples. The carbon content varied due to the addition of activated carbon into the sediment; the measured carbon content met expectations. It was initially proposed that this range of carbon loaded sediments would be used to analyze the effect of carbon content on the bioaccessible fraction of contaminants, but this work was not continued after restructuring of the project goals post the mid-year technical review.

Figure 8. Artificial sediment with varying amounts of activated carbon dosed into the material to understand the effect of carbon content on the bioaccessible fraction of contaminants.

Table 9. The nitrogen and carbon content of the different batches of artificial sediment prepared. The sediment was dosed with activated carbon at varying concentrations ranging from 0.18-1.22% C per gram sediment (1.8-12.2 mg carbon per gram sediment).

Sample	µg N / g sediment	%C (g/g) sediment
Sediment as prepared	BDL	BDL
Carbon Sediment _ A	BDL	0.178 ± 0.027
Carbon Sediment _ B	BDL	0.324 ± 0.088
Carbon Sediment _ C	BDL	0.647 ± 0.031
Carbon Sediment _ D	0.101 ± 0.010	0.958 ± 0.254
Carbon Sediment _ E	0.121 ± 0.005	1.216 ± 0.051

* BDL = below the detection limit; Method detection limit: 100 µg N / g sediment; 0.02 %C g/g (200 µg C / g sediment)

Since the experimental procedure includes the contamination of the sediment with dissolved metals to test metals capture using the passive samplers, the initial metals content of the artificially prepared sediment was analyzed for each sample of sediment using a Teledyne Leeman Labs Prodigy Dual View ICP via microwave digestion (Table 10). The sediment contained a majority of aluminum, iron, and silica, as expected. It should be noted that the sediment was found to have an inherent level of metals found in the sediment. It is important to note that when doing the passive sampling it may be sampling both the endogenous and exogenous sources of metal. It should be noted that the endogenous metal may be mineralized and not available unless acid digested.

Table 10. Initial metals content of the different sediment types prior to artificial contamination. This data provides the baseline for the sediment, which was then spiked with dissolved Cu, Zn, and Pb, and in some situations Ni.

Sediment Sample / Metals (µg/g)	As Prepared	Sediment_A	Sediment_B	Sediment_C	Sediment_D	Sediment_E
P	15.6 ± 2.8	17.5 ± 0.8	16.5 ± 3.0	16.1 ± 1.6	19.2 ± 2.5	16.9 ± 0.9
K	190.3 ± 17.2	162.3 ± 5.5	81.1 ± 4.3	77.9 ± 11.6	53.2 ± 5.2	41.6 ± 7.2
Ca	106.9 ± 36.0	95.9 ± 30.4	106.6 ± 21.5	95.2 ± 30.5	92.2 ± 31.8	127.8 ± 35.7
Mg	21.6 ± 7.7	15.9 ± 1.4	14.6 ± 1.0	17.3 ± 1.0	19.5 ± 2.8	18.6 ± 0.9
S	149.2 ± 14.4	162.1 ± 22.2	162.5 ± 7.2	181.1 ± 7.4	174.7 ± 5.8	194.2 ± 36.6
Al	3535.0 ± 11.2	3493.6±201.2	3358.8±214.8	3446.9±208.0	3535.0±140.1	3573.1±38.8
B	6.0 ± 0.4	5.9 ± 1.0	9.1 ± 5.2	7.4 ± 1.6	8.5 ± 1.5	9.9 ± 2.0
Cu	1.9 ± 0.1	2.1 ± 0.3	2.0 ± 0.1	3.8 ± 1.8	2.0 ± 0.2	2.7 ± 1.1
Fe	232.1 ± 39.6	216.1 ± 15.6	231.8 ± 24.6	290.9 ± 71.7	241.1 ± 22.9	258.0 ± 50.1
Mn	1.36 ± 0.4	1.1 ± 0.0	1.0 ± 0.1	1.4 ± 0.4	1.4 ± 0.1	1.7 ± 0.2
Na	76.1 ± 1.4	79.7 ± 5.6	70.7 ± 10.8	72.4 ± 1.8	77.6 ± 7.6	73.2 ± 6.2
Zn	3.4 ± 3.3	26.6 ± 43.2	2.6 ± 2.7	5.2 ± 4.7	1.4 ± 0.1	14.9 ± 22.4
Ba	7.8 ± 0.4	7.9 ± 0.5	7.2 ± 0.3	7.7 ± 0.4	7.9 ± 0.5	8.5 ± 0.3
Cd	0.3 ± 0.0	0.4 ± 0.2	0.1 ± 0.0	0.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.2
Co	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.1	17.2 ± 24.0	0.3 ± 0.0	0.3 ± 0.0
Cr	3.5 ± 0.0	3.6 ± 0.1	3.4 ± 0.2	7.3 ± 6.3	3.9 ± 0.2	4.7 ± 1.2
Li	7.1 ± 0.4	7.2 ± 0.8	6.5 ± 0.8	6.8 ± 0.5	7.3 ± 0.7	7.5 ± 0.6
Ni	0.8 ± 0.1	0.6 ± 0.0	0.6 ± 0.1	0.9 ± 0.3	0.7 ± 0.1	1.2 ± 0.9
Pb	3.1 ± 0.2	3.3 ± 0.1	3.0 ± 0.2	3.0 ± 0.3	5.6 ± 4.3	3.5 ± 0.6

The sediment samples were held in epoxy lined paint cans that were closed securely with metal lids. The contamination step of the sediment was also identified as a hazardous point of the experimental procedure. To minimize risk of exposure, the cans of contaminated sediment were placed into a secondary container and mixed on a drum roller built in-house for this application (Figure 9).

Figure 9. The tumbler designed and built for the safe and reproducible mixing of contaminants into sediment. This was designed not only to act as secondary containment in case of a spill, but also as a method to effectively mix the aqueous contaminant mixtures into the sediment to ensure a homogeneous composition.

Task 3: Characterize Sediment to Determine Fractions

The artificial sediment prepared and characterized as part of task 2 of this project was divided into 5 kg aliquots into polymeric paint cans. The sediment was artificially contaminated with an aqueous solution of trinitrotoluene, RDX, 1-chlorodibenzo-dioxin, 2,4,8-trichlorodibenzofuran, Cu^{2+}, Zn^{2+}, and Pb^{2+} (100 ppb each). The paint cans were then loaded into a drum (as secondary containment) and rolled on a drum roller to homogenize the samples for 5.7 days (137 hr).

The different fractions, i.e., C_{free}, C_{rev}, and C_{total}, were characterized for the organic contaminants. It is important to understand where contaminants are found in sediments, how source location affects bioavailability, and why passive sample design is critical. Contaminants, with respect to aquatic organism exposure, are either: (i) irreversibly bound to sediment; (ii) reversibly bound, or (iii) freely dissolved. The reversibly bound pool and freely dissolved pool are both bioaccessible whereas irreversibly bound is not. Once homogenized, the sediment was divided into three aliquots. The first aliquot was Soxhlet rinsed with acetonitrile in an attempt to determine C_{total} (total concentration of contaminants). The second aliquot was extracted with butanol to determine C_{rev} (concentration of contaminants reversibly bound to sediment). Finally, the last aliquot was centrifuged to isolate the pore water to determine C_{free} (concentration of contaminants in the pore water).

***(3-1) Quantification of C_{total}*.** Soil samples were divided into 89.5 ± 2.9 g aliquots, which was the maximum amount of sediment that could fit into a cellulose Soxhlet thimble. Each of the three aliquots was Soxhlet rinsed with acetonitrile for 2 hrs. The rinsate was then collected, evaporated, and the contaminants were reconstituted with 2 mL dichloromethane. These samples were analyzed via GC-MS for the TNT, dioxin, and the dibenzofuran. The RDX was analyzed using LC-MS/MS. Quantification was accomplished using calibration curves for each method. The sediment was spiked with an anthracene internal standard to confirm the method. A high concentration of anthracene was observed in the extract showing >80% recovery, indicating the method was valid.

(3-2) Quantification of C_{rev}. The reversibly bound fraction of the organic contaminants was quantified by extraction of 1 g of the wetted sediment with 10 mL butanol for 1 min. The sediment was then filtered away, and the butanol was evaporated. The sample was reconstituted with 0.5 mL dichloromethane. Quantification was done in triplicate. The dichloromethane extracts were analyzed via GC-MS for the TNT, dioxin, and the dibenzofuran. The RDX was analyzed using LC-MS/MS.

(3-3) Quantification of C_{free}. To quantify C_{free}, the pore water needed to be isolated. To accomplish this, enough sediment was centrifuged to achieve 30 mL of the pore water. This was divided into 10 mL aliquots, which were extracted with 1 mL dichloromethane. The 1 mL of the dichloromethane was then evaporated and reconstituted to 100 uL dichloromethane to concentrate the contaminants. The dichloromethane extracts were analyzed via GC-MS for the TNT, dioxin, and the dibenzofuran. The RDX was analyzed using LC-MS/MS.

Task 3 Summary. The percent recovery from each sediment fraction was determined (Table 11). It was found that the dibenzofuran and dioxin were strongly and irreversibly adsorbed to the sediment, as it was not observed in any of the fractions, even the solvent extracted fraction. This was surprising since solvent extraction using Soxhlet systems has been shown to yield high recoveries of PCBs.[58] The artificial sediment was composed of kaolin clay, silt, and silica sand. The high affinity of the dibenzofuran and dioxin was not expected as these materials lack organic content. *However, the very strong binding is interesting from the perspective that kaolin may be useful as a material for sediment remediation acting as an irreversible sink for contaminants.*[59] Kaolin is generally regarded as safe and is a bulk commodity mined in the U.S. Affinity of dioxins to kaolin has been recently documented.[57] Due to this strong affinity for these species for the prepared sediment, it would be unlikely to detect dibenzofurans, and likely PCBs, with the passive samplers. It is also worth note that the explosives are almost exclusively found in the pore water as part of C_{free}. Little adsorption of the explosives to the prepared sediment was expected due to the low $\log K_{\text{ow}}$ of these compounds and the lack of organic matter in the sediment. It was determined that dissolved explosives are ideal contaminants for detection using the Osorb passive samplers.

Table 11. Characterization of the sediment fractions. The dibenzofuran and dioxin were strongly and irreversibly adsorbed to the sediment. The TNT and RDX were found almost exclusively in the pore water.

	% Recovery of Chemical Contaminants from Sediment Fractions			
Analyte	***C*total*** **(total fraction, bound and free)**	***C*rev** **(reversibly bound fraction)**	***C*free** **(fraction in pore water)**	***C*irrev§** **(irreversibly bound fraction)**
TNT	0.1	1.8	10.1	88.0
RDX	0.0	0.0	66.0	34.0
1-chlorodibenzo-dioxin	0.0	0.0	0.0	100.0
2,4,8-trichlorodibenzofuran	0.14	0.13	0.0	99.73

*C_{total} is the amount detected by Soxhlet extraction with acetonitrile.
§C_{irrev} is the amount presumed to be irreversibly adsorbed to sediment as determined by mass balance.

Task 4: Sampler Testing

(4-1: Task 4a) ***Optimization of passive sampler composition for munitions and metals and preparation of new samplers.*** A description of passive sampler optimization is provided above.

(4-2 Task 4b) Determine time to equilibrium for analyte absorption. The goal of this phase of experimentation was to determine the incubation time of the samplers to achieve equilibrium of analyte absorption. Understanding rate of analyte adsorption and time to equilibration is critical to establishing a method to relate concentration in the passive sampler to the concentration in the water stream.

Testing was done in quiescent (unstirred) and flowing (stirred) water samples to determine the effect of water movement on equilibrium time for the samplers. It was hypothesized that passive samplers being deployed in flowing water would have a greater rate of capture due to improved diffusion of the dissolved chemical species towards the samplers. It is important to understand this effect as environmental conditions are uncontrolled. To test this, samplers were immersed in volumes (3.5L) of aqueous solutions containing TNT, RDX, Cu^{2+}, Zn^{2+}, and Ni^{2+} at environmentally relevant concentrations (part-per-billion). Nickel was used in place of lead due to a raw material shortage; nickel was chosen as it is also environmentally relevant. Samplers were removed at 0.5, 1, 2, 4, 8, and 24 hour for the stirred samples and 1, 3, 6, 7, 10, and 14 days for the unstirred samples. Water samples before and after introduction of the passive samplers were then analyzed using standard analytical techniques (TNT and RDX were analyzed using HPLC-UV, metals were analyzed using ICP-AES) to determine percent capture at each time point. The percent capture of the dissolved metals and munitions in the water samples increased with increasing exposure time to the passive samplers (Table 12). Testing was completed in triplicate to give an indication on the repeatability of the testing. Capture of the organic munitions was quite repeatable from sampler to sampler, while greater error between samplers was observed for the dissolved metals. It is hypothesized that this is due to differences in the assembly of the final product, and therefore, the accessibility of the thiol binding groups to the water.

Table 12. Adsorption of RDX, TNT, and dissolved metals from stirred and unstirred solutions. Raw data can be found in Appendix A, Table 3. Measurement involved determining the amount of each analyte remaining in solution after a period of time after passive sampler introduction. Amount captured is reported.

Stirred Samples					
Time points (hr)	**% RDX Capture**	**% TNT Capture**	**% Cu^{2+} Capture**	**% Zn^{2+} Capture**	**% Ni^{2+} Capture**
0.5	0.3 ± 0.0	8.1 ± 0.2	8.3 ± 1.4	2.2 ± 0.7	10.4 ± 2.7
1	2.9 ± 0.0	11.5 ± 1.1	19.8 ± 4.8	22.3 ± 6.1	12.5 ± 3.3
2	5.9 ± 0.1	16.3 ± 1.3	32.8 ± 9.2	31.3 ± 9.9	18.1 ± 6.0
4	9.0 ± 0.3	26.7 ± 3.8	45.9 ± 14.5	35.2 ± 14.7	27.8 ± 11.2
8	11.5 ± 0.3	38.2 ± 3.3	56.4 ± 15.2	38.1 ± 12.9	31.0 ± 14.4
24	14.7 ± 0.5	52.6 ± 12.4	72.0 ± 40.2	42.7 ± 21.1	34.6 ± 21.2
Stagnant Samples					
Time points (days)	**% RDX Capture**	**% TNT Capture**	**% Cu^{2+} Capture**	**% Zn^{2+} Capture**	**% Ni^{2+} Capture**
1	0.0 ± 0.0	0.0 ± 0.0	33.5 ± 3.0	32.2 ± 2.5	25.6 ± 0.8
3	0.5 ± 0.0	6.0 ± 0.2	47.7 ± 5.1	36.8 ± 7.0	41.8 ± 1.6
6	3.1 ± 0.2	11.4 ± 0.2	58.3 ± 8.3	52.3 ± 6.8	56.2 ± 6.6
7	2.0 ± 0.0	10.1 ± 0.3	59.9 ± 7.8	52.5 ± 4.6	58.3 ± 4.0
10	2.8 ± 0.1	20.7 ± 0.5	63.1 ± 9.9	58.5 ± 7.1	61.0 ± 6.9

Also, as expected, the achieved time to equilibrium was faster for stirred water samples compared to quiescent water samples due to the improved mass transfer of the contaminants to the sampler. This is especially true for RDX, which was observed to only have a 4.0% reduction in the water after having the Osorb Passive Samplers in the unstirred water sample for 14 days. This was less apparent with the capture of dissolved metals with the Osorb Passive Samplers (Figure 10). The concentration of each analyte remaining in solution is significantly reduced and begins to level out over time. The passive samplers thus exhibit high affinity and equilibrium sampling. Independently, environmental contaminants atrazine, anthracene, and caffeine were adsorbed to Osorb media. The media was then rinsed with pure water and it was observed the amount of adsorbate deceased with applied water by the same asymptotic trend. (This work was completed in the time after the grant was completed.)

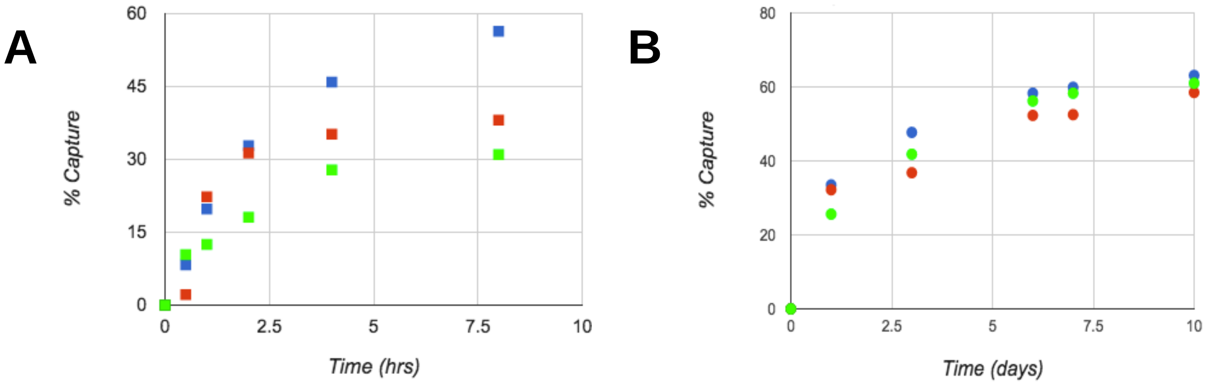


Figure 10. Percent capture of dissolved copper, zinc, and nickel in (A) stirred and (B) unstirred water samples after exposure to Osorb Passive Samplers for varying amounts of time.

These results confirmed initial testing that showed that Osorb passive samplers in water have a fast initial integrating response that comes to equilibrium in less than 48 hr. Data also indicated that mass transfer rates are fast and samplers can respond to transient spikes in analyte concentration on the order of minutes. Samplers were left in stirred water for 48 hr to ensure equilibrium has been reached in all testing going forward. Some sampler-to-sampler variability was noted for metal capture and will be addressed by making the media packing in the mesh holder more homogeneous.

(4-3 Task 4c) Determine sampler response vs. analyte concentration. The effectiveness of the samplers at varying analyte concentrations was examined as a measure of sensitivity. Since munitions and metals are likely to be in the pore water, these experiments were conducted in aqueous solution for the purposes of ease and reproducibility. The goal was to determine how the concentration measured from the passive sampler relates to the pore water concentration.

RDX: Samplers were immersed in solution of varying concentrations of RDX for 24 hr. Sampler response was tested as a function of solution phase concentration at 1.9, 7.5, and 50 ppb RDX. Samplers were tested in triplicate. The bound RDX was extracted with acetonitrile and evaporated down to 2 mL. Samples were run by HPLC-DAD. There was a linear relationship between the RDX found in the extract and the amount in the solution (Figures 11 and 12, Raw data can be found in Appendix A, Table 4). These findings show that the passive samplers have a fast response that is proportion to analyte concentration after a fixed time. Extraction of RDX from seawater was higher than that from deionized water. Affinity of RDX found in seawater is better since the salt in the solution drives the organic components to partition into the hydrophobic Osorb matrix via the “salting out effect”. The total amount of RDX extracted from the 3.5 L volumes by the samplers was 5% for deionized water and 10% for seawater, yielding calibration curve slopes of 86 for deionized water and for 177 for saltwater. The conclusions are *i*) the passive samplers provide two orders of magnitude increase in RDX concentration relative to the concentration in the sampling matrix improving sensitivity and *ii*) deployment in salt water does not lead to interferences, but in contrast, provides improved extraction efficiencies. Osorb media is useful for passive sampling in that it has a high affinity to provide improved signal for the measurement and that it rapidly adsorbs analyte resulting in total amount adsorbed that is proportional to analyte concentration. Assuming the samplers come to equilibrium relatively quickly, the mass captured would be dependent upon the analyte concentration and independent of the the volume sampled.

Experiments were performed in triplicate using separate water containers and samplers. It was found that there was a ~30% relative standard deviation between the recovered RDX from separate samplers. In other words, samplers were binding a different amount of analyte. This variability was also observed in parallel work with pesticides. The lack of reproducibility is attributed to i) the asymmetric design of the sampler which may yield eddy currents when placed in the stirred 3.5 L vessel and ii) variations in how the stainless steel mesh pouches are filled with media. ABS plans to modify the packing of Osorb media in the mesh pouches in the future to make the media packed thinner and more uniformly in the pouch. New sampler geometries may also be evaluated. Long term, sampler-to-sampler variations underscore the need for an improved sampler design or the use of performance reference compounds which is a long-term goal of our passive sampling system.

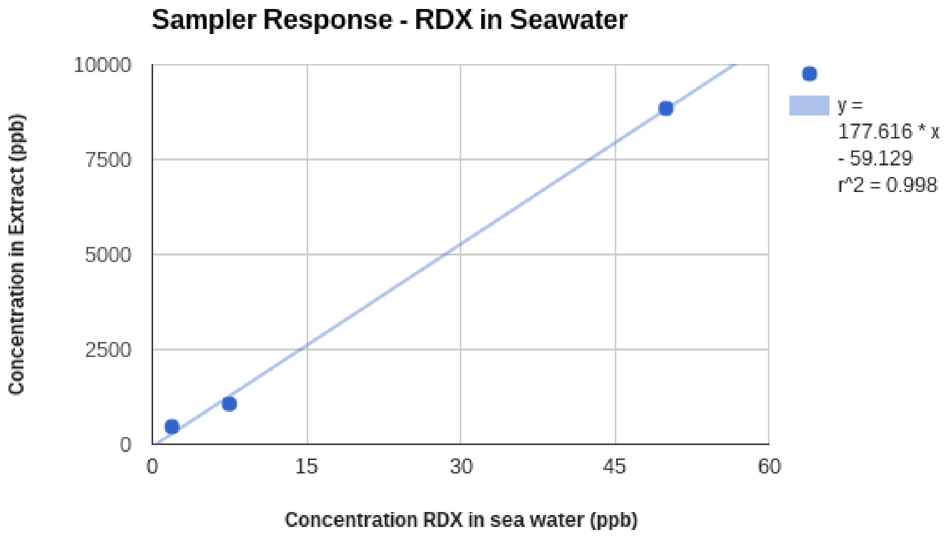


Figure 11: Passive sampler response vs. solution phase concentration for RDX in seawater.

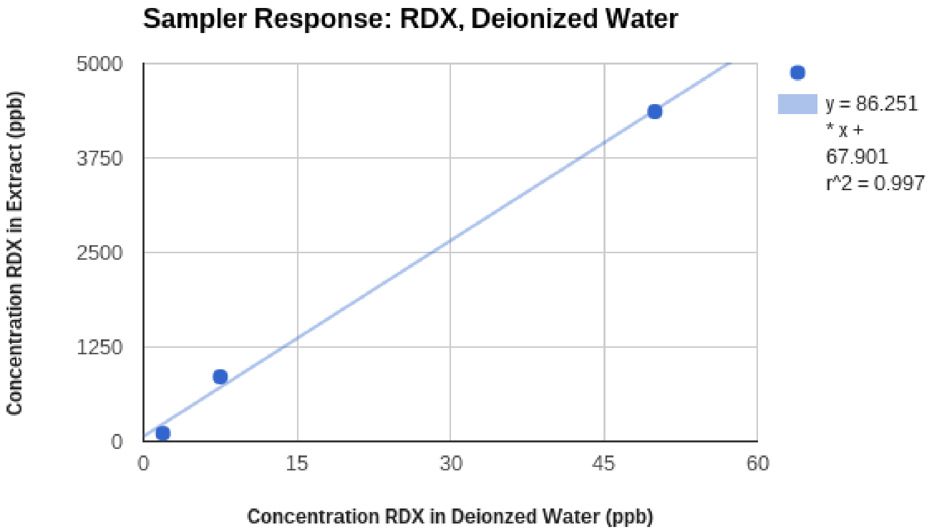


Figure 12: Passive sampler response vs. solution phase concentration for RDX in deionized water.

TNT: Samplers were immersed in solution of varying concentrations of TNT (1.9, 7.5, and 50 ppb) for 24 hr. The testing procedure was hampered by reactions of TNT during the desorption step so the response vs. concentration could not be measured accurately. Specifically, after the bound TNT was extracted with acetonitrile and evaporated down to 2 mL it was found that the acetonitrile extracts turned pink, especially for the seawater samples. Upon investigation it was found that a co-extracted base was deprotonating the TNT. (Reactions with TNT had not been observed before as nanopure Type I DI water had been used for all previous experiments.) Anionic TNT absorbs in the visible and is pink indicating a deprotonation of TNT had occurred in the reaction solution. Moreover, the anion is reactive and can form Meisenheimer complexes with electron rich compounds. Samples were run by HPLC and it was found that >90% of the recovered TNT had been converted to the anion.

As a result, a side project was undertaken to determine the best approach to extract TNT from the passive samplers to prevent deprotonation of the TNT. Three types of elution solvents were tested: i) acetonitrile; ii) acetonitrile with acetic acid, and iii) dichloromethane with acetic acid. The acid was added to neutralize bases and prevent deprotonation reactions. It was found that the acidic dichloromethane was the best extraction solvent for TNT resulting in 88.3% recovery (Table 13). Acetonitrile with acid was also effective. A linear response vs. concentration was observed. The findings allowed for a much better understanding of how to do the analysis when the water matrix is complex and may have interactions with the analyte. From this data, standard operating procedures have been created for sampler placement and extraction allowing user independent laboratories to conduct experiments with Sentinel passive samplers. Due to time constraints, we focused on solving the extraction problem and moved forward with sampling of TNT in sediment (see below).

Table 13. Recovery of TNT with Different Extraction Solvents

Solvent	Percent Recovery
acetonitrile (sample: seawater)	<5
acetonitrile (sample: DI water)	56.1
acetonitrile + acetic acid	62.9
dichloromethane + acetic acid	88.3

***Metals**:* Containers were filled with 3.5 L of chlorine free tap water and simulated sea water. Simulated seawater was prepared following an adapted literature protocol using the commercial product, Instant Ocean®. The water was spiked with Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} at varying concentrations: 0.2, 0.8, 1.9, 7.6, 50 ppb. Samplers were added to each of the water samples, which were left stirring to simulate a fluid water sample, for 48 hr. It was determined in previous tasks of this project that 24 hr is sufficient to reach equilibrium, thus ensuring equilibrium at 48 hours. All testing was done in triplicate.

Recovered metal ion concentration as a function of sampling solution concentration was measured. The binding of metal ions is accomplished through the use of an Osorb media that has surface -SH (thiol) groups. For metals, a number of performance issues were observed. First, for Cu^{2+}, Ni^{2+}, and Pb^{2+} the 6M HCl acid rinse did not extract bound metals well. Here limitations of the sampler chemistry were discovered as recoveries of Cu^{2+}, Ni^{2+}, and Pb^{2+} were all <5%. The poor recovery was determined to be due to the desorption step since it was found that the samplers efficiently extracted the metals from solution. Additional experiments outside the scope of work were performed to try and determine a better means of extraction. First, 6 M nitric acid was used as a potential extraction solvent for metals. Less than 2% recovery was found for nitric acid. ABS Materials has embarked on an expanded set of experiments to find the best extraction system for the metal ion analytes. These results are in progress, however, initial findings indicate that lower concentrations of acid (ex. 1M) provide better metal ion recoveries. Metals are strongly adsorbed, almost irreversibly bound, by the thiolated media. Better metal ion desorption at lower acid concentration seems paradoxical, but may be related to the high concentrations degrading the organosilica. Separate experiments show that the passive sampler media is not able to rebind metals after high concentration acid rinse, indicating some type of degradation. Continued work on finding the best ways to release bound metal ions will be a priority project beyond the scope of this grant.

The one metal ion that was found to be bound and recovered at an extent that allows analysis was zinc(II). Plots of Zn^{2+} in recovered extracts vs. solution concentration are linear (Figures 13 and 14, Raw data can be found in Appendix A, Table 5). However, there is a baseline offset (i.e. the curves do not go through zero). The non-zero intercepts would be indicative of *i*) an additional source of Zn^{2+} that is being bound in the Osorb media capture phase and/or *ii*) incomplete extraction at high binding capacities. Given that the containers are plastic and the stainless steel mesh presumably does not contain zinc there is not an obvious source of trace zinc. Use of Instant Ocean to make seawater likely adds a source of metals. The amount of zinc recovered from seawater samples was higher than the theoretical amount of zinc added exogenously.

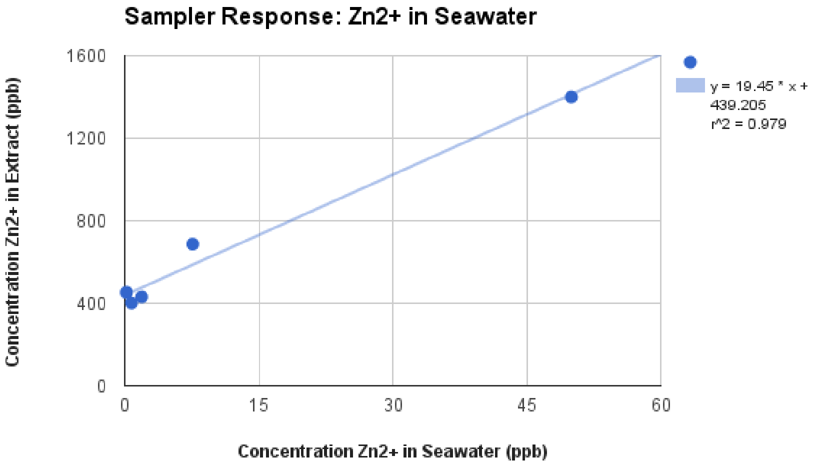


Figure 13: Passive sampler response vs. solution phase concentration for zinc(II) in seawater.

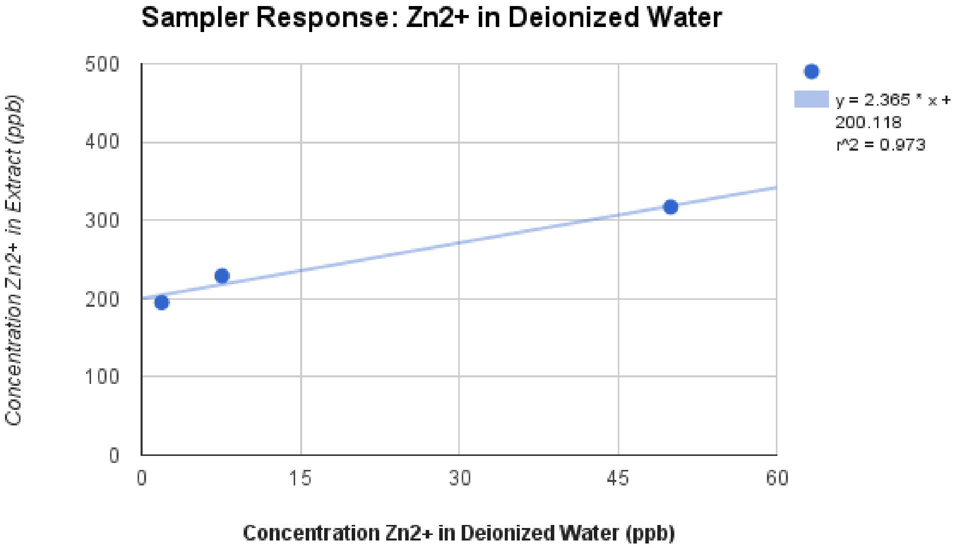


Figure 14: Passive sampler response vs. concentration for zinc(II) in deionized water.

It was concluded based on the results from this phase of testing:

- Linear response for organic analytes was observed.
- Sampler extracts provide two orders of magnitude higher concentration.
- Optimizing desorption methods (ex. for TNT) are as equally critical to adsorption.
- Methods to recovery of metals needs further work, due to strong adsorption interactions.
- There appears to be sinks of metals in the sediment that led to high background.

(4-4: Task 4d) Determine resistance to desorption to determine response characteristics. Variations in the concentration of munitions and metals are likely to vary in seawater due to tidal flow and currents. Initial experiments indicate that Osorb passive samplers will adsorb target analytes quickly allowing for deployment even when analyte concentrations vary rapidly over time. However, back diffusion of analytes when analyte concentrations change from a high to low state may lead to systematically low measurements using passive sampling. The goal of this phase of the grant was to test the back diffusion rates of the organic contaminants by bringing a set of samplers to equilibrium using a high concentration and then soaking them in analyte-free simulated seawater for 1, 3, and 5 days and analyzing the water for the munitions after the desorption period.

The focus of this task was to determine if the organic munitions desorb out of the samplers if introduced into water with no munitions present to mimic field conditions if concentration gradients occur. Desorption testing was not completed for metal ions, as the method of capture differs from that of organic species, with the former being covalent attachment to thiol moieties throughout the media in the samplers and the latter being reversible partitioning into the pores of the media. The standard simulated seawater samples were prepared with 50 ppb each analyte: RDX, TNT, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}. Osorb passive samplers were deployed into 3.5 L samples of the water. The water samples were stirred for the duration of the experiment, 48 hr, which was previously determined as an excess amount of time required for the samplers to come to equilibrium with the water sample. The Osorb passive samplers were then removed from the contaminated water, blotted dry, and resuspended in 3.5 L of simulated seawater, which was kept stirring. The samplers were removed after 1, 3, and 5 days. All work was done in triplicate.

Munitions quantification. Water samples of the initially contaminated water were taken before and after exposure to the Osorb passive sampler. This enabled the amount of munitions that were partitioned into the sampler to be quantified. Due to the low concentration of munitions that are predicted to desorb from the “loaded” passive sampler into the simulated seawater, the water sample was concentrated by passing 1L of the water through an Infinity™ SPE cartridge. The bound munitions to the media within the Infinity SPE cartridge were eluted using acidic DCM, followed by evaporation and reconstitution with 2 mL acetonitrile. The sample was then analyzed using HPLC-DAD (LOD 50 ppb).

The anticipated reduction in RDX and TNT was observed when the samplers were placed in water containing 50 ppb each of the TNT and RDX. As noted before, a variability between the samplers was observed. An average reduction of 33% of the RDX was observed, which resulted in an average loading of 57 μg RDX in each sampler. The Osorb passive samplers show a higher affinity in the capture of TNT compared to RDX, as expected since the sorbent is hydrophobic and TNT has a higher logK_{ow}. Therefore, an average reduction of 74% of the TNT in solution partitioned into the samplers, resulting in an average loading of 130 µg TNT per sampler. Table 14 provides the % reduction, the average micrograms of munition loaded into the samplers, and the quantification of the desorption of these species.

There was no TNT or RDX detected in the simulated seawater after 1, 3, or 5 days of having the preloaded Osorb passive sampler deployed. This indicates that a negligible amount of TNT and RDX desorbed from the Osorb media within the passive sampler into the water, as the limit of detection for this method would be 100 ppt. This is quite promising for the use of these samplers in the field where concentrations may fluctuate dramatically over the course of days or weeks.

Table 14. Quantification of the RDX and TNT extracted from solution into the passive samplers and the amount of munitions desorbed after deployment of the loaded samplers into contaminant-free, simulated seawater for 1, 3, and 5 days. (All testing done in triplicate.)

		RDX	**TNT**
Day 1 Sample Set	% Reduction of munition in water after 48 hr equilibrium	33.0 ± 8.3 %	63.6 ± 3.7%
	µg of munition adsorbed onto passive sampler	58 ± 15	111 ± 7
	amount of munition desorbed into simulated seawater after 1 day*	no detect	no detect
Day 3 Sample Set	% Reduction of munition in water after 48 hr equilibrium	36.3 ± 11.5 %	83.0 ± 6.8 %
	µg of munition pre-loaded into passive sampler	63 ± 20	145 ± 12
	amount of munition desorbed into simulated seawater after 3 days*	no detect	no detect
Day 5 Sample Set	% Reduction of munition in water after 48 hr equilibrium	29.3 ± 20.8 %	76.0 ± 11.3 %
	µg of munition pre-loaded into passive sampler	51 ± 36	133 ± 20
	amount of munition desorbed into simulated seawater after 5 days*	no detect	no detect

* Limit of detection: 100 ppt

It was concluded based on the results from this phase of testing:

- Neither the TNT nor the RDX that was initially adsorbed from water was desorbed from the passive samplers over the course of five days in stirring simulated seawater. This confirms that the samplers can be used in water streams or sediment where currents lead to variations in the concentration over time without underestimation of the amount of contaminants due to loss via desorption.
- As previously observed, the Osorb passive samplers have approximately twice the affinity to extract TNT from water compared to RDX. Results not shown here indicate that the affinity is directly proportional to an adsorbate's $\log K_{ow}$.

Task 5: Use of passive samplers in sediment.

The objective of task 5 was to test the passive samplers in artificially contaminated sediment. Sediment, as prepared in task 3, was doped with the analytes of interest (Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, TNT, and RDX) at varying concentrations. The temperature, depth of penetration of the samplers into the sediment, and the incubation time was held constant. The pore water for each applied concentration was fully characterized for munition and metal content. After incubation, the sequestered chemicals within the Osorb passive samplers were recovered using standard extraction methods for both the munitions and metals to understand the correlation of the applied concentration to the absorbed concentration.

Preparation of the Sediment: Artificial sediment (5 kg) was contaminated by adding 1 L of aqueous TNT, RDX, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} in deionized water to polymeric paint cans. The aqueous solution of contaminants was adjusted to 0.5 mM HCl, to prevent precipitation of the metal salts, primarily the Pb^{2+}. As noted before, the sediment was mixed continuously for 5.5 days to produce a homogeneous sample. Five sets of sediment were prepared in triplicate with 250 ppb, 100 ppb, 50 ppb, 25 ppb, and 10 ppb of each contaminant. A control sediment sample was also prepared for each concentration to quantify the amount of contaminant that irreversibly adsorbs to the sediment itself. No sampler was added to the control sediment.

Analysis of the pore water: The sediment in each can was centrifuged to recover 15 mL of the pore water. The water was split and one fraction was analyzed for metal content via ICP-AES, while the other was analyzed for TNT and RDX using HPLC-UV.

Figure 15 shows the concentration of the RDX and TNT in the pore water versus the applied concentration. Adsorption to the sediment was stronger for the more non-polar TNT compared to the RDX. The overall C_{free} of the TNT was 90-95% less than the concentration initially added due to adsorption to the sediment and the unavailability to be sampled. Overall C_{free} of the RDX was less impacted by adsorption to the sediment, where 20% was bound. Interestingly, the percentage of the RDX adsorbed by the sediment increased as the applied concentration increased. The average fraction of the RDX adsorbed to the sediment was 22%, while the average fraction of the TNT adsorbed to the sediment was 96%.

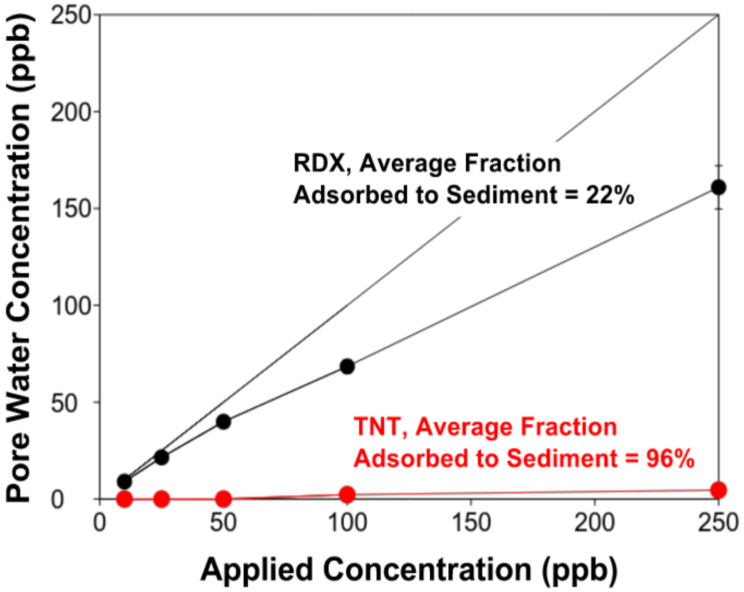


Figure 15. The concentration of RDX and TNT in the pore water versus the applied concentration. The TNT is more strongly adsorbed to the sediment than the RDX. The amount of RDX adsorbed to the sediment increases with increasing concentration.

The metal concentration was also observed to be quite low in the pore water, indicating substantial adsorption of the metal ions to the sediment (Table 15). The exogenous Cu^{2+} and the Pb^{2+} added in the water fully adsorbed to the sediment, even at the highest concentration applied (250 ppb). The majority of the Zn^{2+} and the Ni^{2+} also adsorbed to the sediment, however, detectable free metal was observed in the pore water at higher applied concentrations. In general, sediment has capacity to adsorb dissolved metals and also appears to have natural amounts of various metals. As noted in previous analysis of the sediment, it is inherently composed of these four metal species at a part-per-million level, and that may act as a source of the metals within the samples.

Table 15. The concentration of the metal ions in the pore water and the sediment.

Concentration of Metals in Solution Added to Sediment	**Metal Concentration Measured in Pore Water Post Exposure to Sentinel Passive Samplers**			
	Cu (ppb)	**Zn (ppb)**	**Ni (ppb)**	**Pb (ppb)**
10 ppb metals	< 2 ± 0	5 ± 1	21 ± 4	< 4 ± 0
25 ppb metals	< 2 ± 0	7 ± 1	28 ± 5	< 4 ± 0
50 ppb metals	< 2 ± 0	9 ± 2	245 ± 177	< 4 ± 0
100 ppb metals	< 2 ± 0	11 ± 2	181 ± 247	< 4 ± 0
250 ppb metals	< 2 ± 0	9 ± 3	138 ± 156	< 4 ± 0
Digested sediment	1900 ± 100	3400 ± 3330	800 ± 100	3100 ± 200

Extraction of the Samplers: Passive samplers were inserted at consistent depth (~6 in), one sampler per can. The samples were left at room temperature for 2 weeks. After 2 weeks, the passive samplers were removed from the sediment, rinsed with nanopure water, and excess water was removed with a Kimwipe. (Note: Work in Task 4 determined that bound analytes are not desorbed when placed in water or seawater so the rinse step would not liberate any bound explosives or metals). The organic contaminants absorbed by the sorbent within the samplers were extracted by submerging the stainless steel sampler into 10 mL acidic acetonitrile (100 uL acetic acid in 10 mL acetonitrile) for 1 min and then repeating the process for a total of three extractions. (The acid is used to prevent deprotonation of TNT.) The extracts were combined into a tube and evaporated to dryness and reconstituted in 2 mL of acetonitrile. After filtration, the munitions were analyzed via HPLC-UV and GC-MS using calibration curves for quantification.

A linear correlation between the concentration of the RDX and TNT in the sampler extract was observed relative to the amount of total applied contaminant (Figure 16, raw data can be found in Appendix A, Table 6). In other words, the sorbent was sampling both the fraction of analyte in the pore water and the fraction irreversibly bound to the sediment. It appears the Osorb media based passive samplers act as a hydrophobic adsorptive sink for contaminants accessing both free and bound contaminants. The adsorptive capacity of the sampler may be ideal in mimicking the uptake of contaminants by benthic organisms. Thus, these samplers may provide a unique tool for site evaluation purposes. Pore water concentration of contaminants is normally used to make an evaluation in combination with modeling based on sediment parameters. Osorb passive samplers may provide a new type of "environmental concentration" by assessing the total bioavailable amount since the particles acts as a sink like biological tissue. What remains to be determined is how closely Osorb passive samplers mimic tissue of benthic organisms.

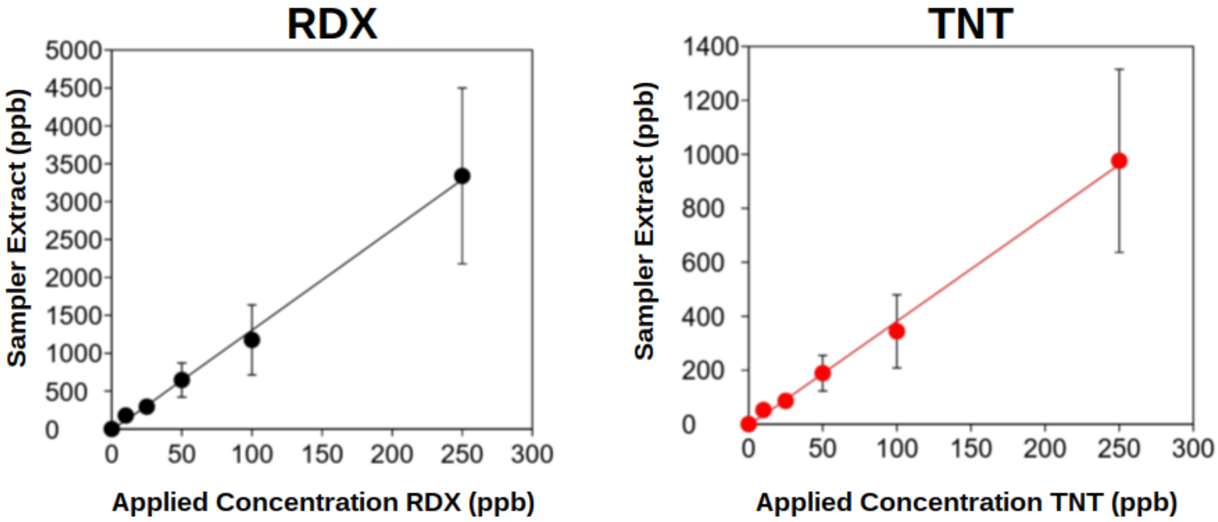


Figure 16. The concentration of RDX and TNT in the sampler extract relative to the applied concentration of each munition. The concentration captured is proportional to the applied volume of the contaminants, not the amount available in the pore water.

Validating the hypothesis. It is important to note that the “applied concentration” of RDX or TNT is the concentration in the water prior to addition to the sediment. A significant amount of both compounds was adsorbed by the sediment after the solution was applied. For example, >95% of the TNT was removed from the pore water. Calculating the mass of TNT, 1.9 μg was adsorbed from the 250 ppb dosed sediment. Given the pore water concentration, that mass of extracted TNT would be obtained from extracting 20% of all the pore water in the can, if no desorption from sediment was occurring. Over a time of 2 weeks without any stirring, the rate of diffusion is insufficient to explain the mass loading if TNT was adsorbed exclusively from the pore water. ***Therefore, the mass balance calculations indicate that the media in the sampler acts as a sink for TNT sampling both the pore water and the reversibly bound fraction of TNT on the sediment.*** If the affinity of the adsorption mimics biological tissue, then the sampler would be measuring the bioaccumulation potential directly. The ability of the Osorb Passive Samplers to act as a sink for both dissolved metals and organics may be a mechanism that allows for a direct measurement of bioaccumulation of contaminants.. Although further experiments are needed, it is hypothesized that the ability of the sampler to both measure C_{free} and C_{rev} is due to *i*) the high capacity of the swellable media; *ii*) the direct contact between the media and the sediment; and *iii*) the mechanical flexibility of the sorbent which sheds biofilms and prevents particle pore blocking. If the samplers are measuring the bioaccumulation of contaminants, such a measurement would be valuable for site assessments.

Metals. The passive samplers have the ability to simultaneously adsorb organic analytes, such as munitions, and metals. After the organics have been removed by acetonitrile rinse, metals were extracted in a subsequent step by first drying the samplers, cutting open the stainless steel pouch, and recovering the sorbent media. The Osorb media was placed into empty SPE cartridges, and the metals were dissociated by flushing with two aliquots of 1 mL HCl (6 M). The acidic solution that passed through the media was collected and diluted to 1.2 M HCl with nanopure water. Metal content was analyzed using ICP-AES.

Extraction of the metals from the samplers showed significant amounts of captured metals (Table 16) despite the low concentrations of metals in the pore water. The high endogenous amount of metals in the sediment itself led to a large background amount of metal ions captured by the passive samplers. These data demonstrate that the passive samplers are measuring both the free and sediment-bound fraction of metals by offering a sink of high affinity biomimetic adsorption sites (thiol groups). Osorb media based passive samplers thus hold the potential to offer a new paradigm in site evaluation to directly measure the impact on organisms that have sufficient mass to accumulate metals and organic contaminants.

Table 16. The concentration of the metal ions extracted from the passive samplers using acid to desorb the adsorbed metal species.

Concentration of Metals in Solution Added to Sediment	**Metal Concentration Extracted from Sentinel Passive Sampler Using Strong Acid Rinse**			
	Cu (ppb)	**Zn (ppb)**	**Ni (ppb)**	**Pb (ppb)**
10 ppb metals	785 ± 1061	425 ± 401	1315 ± 2222	13 ± 10
25 ppb metals	631 ± 896	283 ± 338	1724 ± 2909	11 ± 2
50 ppb metals	8486 ± 4933	4137 ± 3369	9446 ± 5252	59 ±72
100 ppb metals	2409 ± 3830	878 ± 1315	1925 ± 3128	7 ± 2
250 ppb metals	12213 ± 20961	7351 ± 12376	2861 ± 4882	12 ± 1

The passive samplers captured significant amounts of metals compared to the amounts applied in the dosing solution. It is apparent that there are: *i*) metals naturally present in the materials used to create the sediment; and *ii*) the passive sampler acts as a strong sink for these metals. In fact, mass of metals captured exceeds what is present in the pore water, therefore, the thiol groups in the Osorb media are a strong sink sampling primarily from C_{rev} fraction. ***If the media we created is indicative of binding affinity of cysteine residues in biological tissue, then these results indicate that measurement of metals in pore water is insufficient to understanding exposure to benthic organisms.*** Clay in the sediment acts as a natural sink for metals, but it appears that metals are not irreversibly adsorbed when competing for adsorption with thiols.

There were some additional observations. First, recovery of lead was low. It is presumed that the samplers irreversibly adsorb Pb^{2+} (i.e., the K_{sp} for PbS is $3x10^{-38}$). An alternative to acid extraction, such as full digestion, will likely be required for the analysis and quantification of Pb^{2+}. Second, the concentration of metals extracted was quite variable with standard deviations often greater than the mean. Variability may be attributed to heterogeneity in the sediment, however, it is likely that the extraction rate may differ between samplers. Strong binding affinity may magnify small differences in sampler construction where some samplers yield better physical contact between the media granules and the sediment. ABS Materials has thus been motivated to make the sampler design more consistent and has achieved a better design that can be implemented in the future for metals analysis.

It was concluded based on the results from this phase of testing:

- There is linear correlation between the concentration of contaminants measured by the samplers relative to the applied mass of contaminant. Linear behavior reduces the complexity in relating measured concentration to environmental concentration.
- Mass balance indicates that Osorb media is an adsorption sink measuring C_{free} and C_{rev}.
- The samplers demonstrate a strong affinity for metal ions. The samplers were observed to capture endogenous metals, likely from the sediment. If the media is indeed biomimic,

these findings would indicate that pore water measurements of metals would substantially underestimate metal ion exposure of benthic animals.

- The strong binding between the thiol groups decorating the sorbent media and the dissolved metals results in challenges desorbing the metal ions for quantification. It is proposed that full digestion of the media would lead to better recovery of metals.

Testing with US Navy. Samplers were provided to Dr. Gunther Rosen (US Navy) who was testing the use of passive samplers to detect the dissolved compounds from an unexploded ordnance under a separate SERDP project. The samplers were used in the flume experiments conducted at ERDC in 2015. The analysis of the samplers was completed by Dr. Jason Belden at Oklahoma State University. The Sentinel samplers sent to Dr. Rosen were placed in a flume inside and outside POCIS sampling cages. The samplers were used to adsorb and measure RDX, TNT, 2,4-dinitrotoluene and 2,6-dinitrotoluene (Figure 17) at different flow rates. Initial findings are that the Sentinel sampler had a significantly higher final loading of TNT compared to POCIS. Sampling rates were less for RDX, which is more polar. The mass (ng) of munitions in the Osorb media for each flow rate can be found in Appendix A, Table 7.

A set of Sentinel passive samplers were placed outside the POCIS cages (Figure 18) where they would be directly in the flume current. When placed outside the cage the sampling rates (amount of analyte capture as a function of time) were 10x higher than inside the cage (Table 17). Lower sampling rates inside the cage is likely due to disruption of flow by the metal mesh. In fact there appears to be a threshold flow rate between 5-10 cm/s where water can overcome the frictional forces of the holes in the stainless steel mesh of the POCIS cage. We did not receive any data from the Jason Beldon (Oklahoma State) laboratory or the Navy on how Osorb samplers compared with POCIS, however, we were told that Osorb had higher sampling rates.

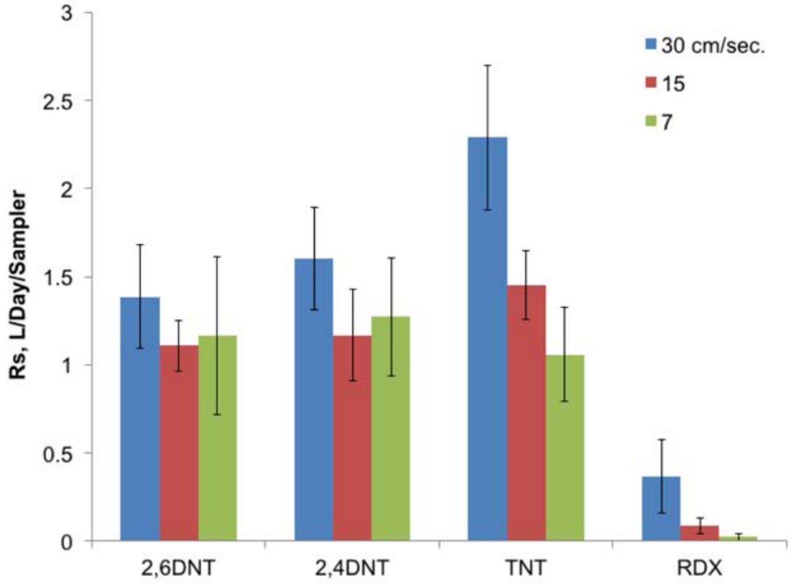


Figure 17: Sampling rate of Sentinel passive samplers deployed inside a POCIS canister in the ERDC flume. (Figure produced by Dr. Jason Beldon, Oklahoma State University, who conducted the deployment and analysis.)

Figure 18. POCIS canister. Sentinel sampler were placed inside and outside the mesh.

Table 17. Update rates of Sentinel passive samplers placed inside and outside the POCIS canister/cage.

Analyte	Sampling Rate L/day		Ratio (out/in)
	Inside cage	Outside cage	
TNT	0.064 ± 0.021	1.06 ± 0.26	16.6
2,4-DNT	0.103 ± 0.023	1.27± 0.34	12.3
2,6-DNT	0.101 ± 0.034	1.16 ± 0.44	11.6
RDX	0.003 ± 0.001	0.023 ± 0.020	7.4

The dependence of the amount of TNT and RDX captured on the flow rate indicates that there is a barrier to mass flux into the Osorb media at lower flow rates. A flow rate dependence was particularly observed for RDX which has the lowest $\log K_{ow}$ and lowest affinity to the Osorb media. The Osorb passive sampler design is based on a stainless steel pouch filled with media. It is packed in a way that the media is not a thin layer, but where media particles settle into ~5-10 mm thick bed at the bottom of the pouch. Although our initial design is easy to make, the media on the outside of the bed may disrupt flow to the particles of Osorb deeper inside the sampler. A more optimal passive sampler design may be needed if sampling water that is flowing to ensure consistent results. A better design is to use a thinner bed across the membrane and prevent settling in the stainless steel pouch.

Task 6: Conclusions and Implications for Future Research

The major objectives of this project were completed. A multi-analyte passive sampler with high affinity for a wide range of polar and non-polar organics and metals has been developed. The major conclusions are the following.

1) Samplers were developed that have high affinity for both metals and organic compounds. The affinities are generally high and the capacities are large enough that the Osorb media particles can act as an adsorptive sink, thus sampling analytes from both the pore water and those molecules reversibly adsorbed to sediment. Sampling in this way may be a paradigm shift since traditional site assessments rely on measurements of pore water concentration. If the affinities of the Osorb media match that of benthic organisms, then the samplers can be used as a direct measurement of biological impact.
2) Metal ion binding to thiol groups is very strong and generally non-specific. Affinity of organic compounds to hydrophobic Osorb media is directly related to $\log K_{\mathrm{ow}}$. Metal ion binding is very strong preventing quantitative desorption by acid. Complete microwave digestion of the media is recommended in future work.
3) Initially we hypothesized that the samplers were integrative for organic compounds, but upon further analysis, the evidence strongly suggests that Osorb passive samplers are governed by equilibrium with fast adsorption kinetics and slow desorption (see below). Osorb samplers are pseudo-integrative for metal ions due to the strong thiol-metal binding.
4) The Osorb passive sampler design using a stainless steel mesh pouch is simple to manufacture and allows direct contact of media with sediment. The sampler design is easy to use and standard protocols have been developed so third party testing laboratories can complete the analysis. However, the sampler design needs improvement, especially if used in flowing water where inter-sampler variability was high and dependence on the flow rate was observed. Future designs will incorporate a thinner bed of Osorb particles across the mesh surface that allows direct contact with the water.
5) Sediment was created by the mixture of various minerals so as to start with a clean matrix to which known amounts of contaminants could be added. By doing so, it was found that kaolin clay and silt are effective in irreversibly adsorbing chlorinated polyaromatic compounds. In fact, the adsorption is so strong that solvent extraction is insufficient to remove bound 1-chlorodibenzo-dioxin and 2,4,8-trichlorodibenzofuran. These materials may be useful to explore for site remediation studies.

Integrative or Equilibrium Based Sampling? Review of the data obtained during this project in addition to testing outside the tasks here has shown that for dissolved organic compounds Osorb passive samplers appear governed by equilibrium. Equilibrium sampling is supported by several pieces of evidence. First, a steady-state concentration is reached in experiments shown above where a sampler is placed in a fixed volume of water. Second, in separate experiments with other environmental contaminants (not part of this study) a slow desorption of adsorbed organic compounds is observed when the samplers are continuously rinsed with deionized water following adsorption. Third, a separate study was conducted by a third party which evaluated Osorb samplers in using a controlled flow system with pulsed introduction of organic solutes.[60] Data, which measured sampling performance for 36 different water solutes, showed that Osorb media was not integrative whereas Oasis HLB and Dowex Optipore L-493 were both integrative (with essentially irreversible adsorption of organic compounds from water under the experimental conditions for Oasis HLB and Dowex.)

There are unique aspects of the sampling performance of Osorb media. First, the rates of analyte adsorption are much faster than the desorption. Fast adsorption to reach equilibrium is very useful in sampling short duration events. Second, Osorb media exhibits a high capacity, which allows for a wide dynamic range. There is a linear response in the concentration adsorbed to the amount in solution. After equilibrium has been reached, it is relatively simple to determine the concentration in the aqueous phase. Finally, the affinities to adsorb organic compounds is relatively strong, despite being reversible. Notably, the binding affinity of Osorb media generally matches that of Oasis HLB, but Osorb media has a slow desorption rate that makes the response of Osorb passive based on equilibrium.

Moving forward, we see two potential follow-up projects. The preferred project is to collaborate with a site where stormwater and/or groundwater may be a source for sediment (re-) contamination. Data from the project herein indicates that the Sentinel passive sampler has the capability of measuring contaminants in short duration flows due to the fast uptake kinetics. We envision deploying a set of samplers across multiple locations and obtaining a geospatial snapshot of contaminants in a first flush event. To our knowledge, no such study has ever been performed. A second potential follow-up project would be to assess how biomimic the adsorption to Osorb media is compared to benthic fish. The PI is currently collaborating with Dr. Heiko Shoenfuss at St. Cloud State University who is an environmental biologist that could assist in such studies.

References Cited:

1. Vrana, Branislav, Ian J. Allan, Richard Greenwood, Graham A. Mills, Ewa Dominiak, Katarina Svensson, Jesper Knutsson, and Gregory Morrison. "Passive sampling techniques for monitoring pollutants in water." *TrAC Trends in Analytical Chemistry* 24, no. 10 (2005): 845-868.
2. Mayer, P., Tolls, J., Hermens, J. L., & Mackay, D. (2003). Peer reviewed: equilibrium sampling devices. *Environmental science & technology*, 37(9), 184A-191A.
3. Stuer-Lauridsen, F. (2005). Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. *Environmental pollution*, 136(3), 503-524.
4. Cornelissen, G., Arp, H. P. H., Pettersen, A., Hauge, A., & Breedveld, G. D. (2008). Assessing PAH and PCB emissions from the relocation of harbour sediments using equilibrium passive samplers. *Chemosphere*, 72(10), 1581-1587.
5. Vinturella, Amy E., Robert M. Burgess, Brent A. Coull, Kimberly M. Thompson, and James P. Shine. "Use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes." *Environmental science & technology* 38, no. 4 (2004): 1154-1160.
6. Hawthorne, S. B., Miller, D. J., & Grabanski, C. B. (2009). Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Analytical chemistry*, 81(22), 9472-9480.
7. Oen, A. M., Janssen, E. M., Cornelissen, G., Breedveld, G. D., Eek, E., & Luthy, R. G. (2011). In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environmental science & technology*, 45(9), 4053-4059.
8. Tomaszewski, J. E., & Luthy, R. G. (2008). Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. *Environmental science & technology*, 42(16), 6086-6091.
9. Adams, R. G., Lohmann, R., Fernandez, L. A., MacFarlane, J. K., & Gschwend, P. M. (2007). Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environmental science & technology*, 41(4), 1317-1323.
10. Gschwend, P. (2008). New Tools for Assessing Organic Contaminants in Sediments: Can We Use Passive Sampling to Identify Hazardous Deposits?. In SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, Dec (pp. 2-4).
11. Fernandez, L. A., MacFarlane, J. K., Tcaciuc, A. P., & Gschwend, P. M. (2009). Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. *Environmental science & technology*, 43(5), 1430-1436.
12. Kot-Wasik, A., Zabiegała, B., Urbanowicz, M., Dominiak, E., Wasik, A., & Namieśnik, J. (2007). Advances in passive sampling in environmental studies. *Analytica chimica acta*, 602(2), 141-163.

13. Hawthorne, S. B., Jonker, M. T., van der Heijden, S. A., Grabanski, C. B., Azzolina, N. A., & Miller, D. J. (2011). Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Analytical chemistry*, 83(17), 6754-6761.

14. Lohmann, R. (2011). Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environmental science & technology,* 46(2), 606-618.

15. Booij, K., Sleiderink, H. M., & Smedes, F. (1998). Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environmental Toxicology and Chemistry*, 17(7), 1236-1245.

16. Kraaij R, Mayer P, Busser F.J.M, Bolscher M.V, Seinen W, Tolls J. (2003). Measured pore-water concentrations make equilibrium partitioning work—A data analysis. *Environmental science & technology* 37:268–274.

18. Zeng, E. Y., & Noblet, J. A. (2002). Theoretical considerations on the use of solid-phase microextraction with complex environmental samples. *Environmental science & technology*, 36(15), 3385-3392.

19. Parkerton, T. F., Stone, M. A., & Letinski, D. J. (2000). Assessing the aquatic toxicity of complex hydrocarbon mixtures using solid phase microextraction. *Toxicology letters*, 112, 273-282.

20. Witt, G., Lang, S. C., Ullmann, D., Schaffrath, G., Schulz-Bull, D., & Mayer, P. (2013). Passive Equilibrium Sampler for in Situ Measurements of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments. *Environmental science & technology*, 47(14), 7830-7839.

21. Burkett, C. M., Underwood, L. A., Volzer, R. S., Baughman, J. A., & Edmiston, P. L. (2008). Organic–inorganic hybrid materials that rapidly swell in non-polar liquids: nanoscale morphology and swelling mechanism. *Chemistry of materials*, 20(4), 1312-1321.

22. Huckins, J. N., Manuweera, G. K., Petty, J. D., Mackay, D., & Lebo, J. A. (1993). Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environmental science & technology*, 27(12), 2489-2496.

23. Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K. (1990) Semipermeable Membrane Devices Containing Model Lipid: A New Approach to Monitoring the Bioavailability of Lipophilic Contaminants and Estimating Their Biocentration Potential. *Chemosphere*, *20*, 533-552.

24. Booij, K., Sleiderink, H. M., & Smedes, F. (1998). Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environmental Toxicology and Chemistry*, 17(7), 1236-1245.

25. Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., Von Gunten, U., & Wehrli, B. (2006). The challenge of micropollutants in aquatic systems. *Science*, 313(5790), 1072-1077.

26. Reichenberg, F., & Mayer, P. (2006). Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental toxicology and chemistry*, 25(5), 1239-1245.

27. Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., et al, & Paquin, P. R. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental toxicology and chemistry*, *10*(12), 1541-1583.

28. Mayer, P., Parkerton, T. F., Adams, R. G., Cargill, J. G., Gan, J., Gouin, T., Escher, B. I. (2013). Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integrated environmental assessment and management*.

29. Jonker, M. T., & Koelmans, A. A. (2002). Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environmental science & technology*, 36(17), 3725-3734.

30. Cornelissen, G., Rigterink, H., ten Hulscher, D. E., Vrind, B. A., & van Noort, P. (2001). A simple Tenax® extraction method to determine the availability of sediment -sorbed organic cor *Environmental Toxicology and Chemistry*, 20(4), 706-711.

31. Fux, E., Marcaillou, C., Mondeguer, F., Bire, R., & Hess, P. (2008). Field and mesocosm trials on passive sampling for the study of adsorption and desorption behaviour of lipophilic toxins with a focus on OA and DTX1. *Harmful Algae*, 7(5), 574-583.

32. Gouliarmou, V., & Mayer, P. (2012). Sorptive bioaccessibility extraction (SBE) of soils: combining a mobilization medium with an absorption sink. *Environmental science & technology*, 46(19), 10682-10689.

33. Cui, X., Mayer, P., & Gan, J. (2013). Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations, and limitations. *Environmental Pollution*, 172, 223-234.

34. Loy, D. A.; Shea, K. J. Bridged polysilsesquioxanes. Highly porous hybrid organic-inorganic materials. *Chem. Rev.* 1995, *95*, 1431-1442.

35. Cerveau, G.; Corriu, R. J. P.; Framery, E. Nanostructured organic-inorganic hybrid materials: Kinetic control of the texture. *Chem. Mater.* 2001, *13*, 3373-3388.

36. Cerveau, G.; Corriu, R. J. P., Fischmeister-Lepeytre, C. Influence of kinetic parameters on the textural and chemical properties of silsesquioxane materials obtained by sol-gel process. *J. Mater. Chem.* 1999, *9*, 1149-1154.

37. Edmiston, P.L.; Campbell, D.P.; Gottfried, D.S.; Baughman, J.; Timmers, M.M. Detection of trinitrotoluene in the parts-per-trillion range using waveguide interferometry, *Sensors & Actuators B.* 2010, *143*, 574-582.

38. Walker, N. R.; Linman M. J.; Timmers, M. M.; Dean S. L.*; Burkett, C. M.; Lloyd, J. A.; Keelor, J. D.; Baughman, B. M.; Edmiston, P. L.. Selective detection of gas-phase TNT by integrated optical waveguide spectrometry using molecularly imprinted sol-gel sensing films. *Analytica Chimica Acta*, 2007, *59*3, 82-91.

39. Carlson, C. A.; Lloyd, J. A.; Dean, S. L.; Walker, N. R., Edmiston, P. L. Sensor for fluorene based on the incorporation of an environmentally sensitive fluorophore proximal to a molecularly imprinted binding site, *Anal. Chem*., 2006, *78*(11), 3537 -3542.
40. Hoffmann, F., Cornelius, M., Morell, J., & Fröba, M. Silica-based mesoporous organic–inorganic hybrid materials. *Angew. Chemie Int. Ed*., 2006, *45*(20), 3216-3251.
41. Rebbin, V.; Schmidt, R.; Fröba, M. Spherical particles of phenylene-bridged periodic mesoporous organosilica for high-performance liquid chromatography. *Angew. Chemie Int. Ed*., 2006, *45*(31), 5210-5214.
42. Burkett, C. M.; Underwood, L. A., Volzer, R. S.; Baughman, J. A.; Edmiston, P. L. Organic-inorganic hybrid materials that rapidly swell in non-polar liquids: Nanoscale morphology and swelling mechanism. *Chem Mater.* 2008, *20(4),* 1312-1321.
43. Fujita, S. Inagaki, S. Self-organization of organosilica solids with molecular-scale and mesoscale periodicities. *Chem Mater.*, 2008, *20*(3), 891-908.
44. Sayari, A.; Wang, W. Molecularly ordered nanoporous organosilicates prepared with and without surfactants. *J. Am. Chem. Soc*., 2005, *127*(35), 12194-12195.
45. Trammell, S. A.; Zeinali, M.; Melde, B. J.,; Charles, P. T.; Velez, F. L.; Dinderman, M. A.; Markowitz, M. A. Nanoporous organosilicas as preconcentration materials for the electrochemical detection of trinitrotoluene. *Anal. Chem*., 2008, *80*, 4627-4633.
46. Graham, A. L.; Carlson, C. A.; Edmiston. P. L. Development and characterization of molecularly imprinted sol-gel materials for the selected detection of DDT. *Anal. Chem*. 2002, *74*, 458-467.
47. Edmiston, P. L.; Underwood, L. A. Absorption of dissolved organic species from water using organically modified silica that swells. *Sep. & Purif. Tech.*, 2009, *66*, 532-540.
48. Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. Porous polysilsesquioxanes for the adsorption of phenols. *Environ. Sci. Technol*. 2002, *36*, 2515-2518.
49. Burkett, C. M.; Edmiston P. L.; Highly swellable sol-gels prepared by chemical modification of silanol groups prior to drying. *J Non-Crystalline Solids*, 2005, *351*, 3174-3178.
50. Edmiston, P.L.; Jolly, S. Nanoengineered Organosilica Materials for the Treatment of Produced Water. In *Aquananotechnology*, Ed. David Reisner, 2014: CRC Press, Boca Raton, FL in press.
51. Edmiston, P. L., Keener, J., Buckwald, S., Sloan, B., Terneus, J. Flow Back Water Treatment Using Swellable Organosilica Media. SPE Eastern Regional Meeting, 17–19 August 2011, Columbus, Ohio, USA. 148973-MS DOI 10.2118/148973-MS (2011).
52. US Patent 7,790,830. “Swellable sol-gels, methods of making, and use”
53. Atkinson, M. J.; Bingman, C. Elemental composition of commercial seasalts. *J. Aquariculture Aquat. Sci*. 1998, 8, 39-43.
54. Suedel, B. C.; Rodgers, Jr., J. H. *Environ. Tox. Chem*. 1994, 13, 1163-1175.
55. Environmental Protection Agency. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates. EPA 600/R-99/064. Washington, D.C., March 2000.

56. Beller, H. R., and Kevin T. Use of liquid chromatography/tandem mass spectrometry to detect distinctive indicators of in situ RDX transformation in contaminated groundwater. *Environ. Sci. Technol*. 36.9, 2002, 2060-2066.

57. Horii, Y.; Ohtsuka, N.; Minomo, K.; Nojiri, K.; Kannan, K.; Lam, P. K. S.; Yamashita, N. Distribution, characteristics, and worldwide inventory of dioxins in kaolin ball clays. *Environ. Sci. Technol.,* 45, 2011, 7517-7524.

58. Jonker, M. T., Koelmans, A. A. Extraction of polycyclic aromatic hydrocarbons from soot and sediment: solvent evaluation and implications for sorption mechanism. *Environmental science & technology*, 2002, 36(19), 4107-4113.

59. Fogler, H. S., Srinivasan. K.R. "Modified clay sorbents." U.S. Patent 4,740,488, issued April 26, 1988.

60. Morrison, S.A., . Belden, J.B.. Calibration of nylon organic chemical integrative samplers and sentinel samplers for quantitative measurement of pulsed aquatic exposures."*Journal of Chromatography A* 1449, 2016. 109-117.

Appendix A: Raw Data

Table A-1. Capture of dissolved metals using various Osorb medias. (Top) Capture of Cu^{2+}, Zn^{2+}, and Pb^{2+} in individual samples; (bottom) capture of dissolved metals from a mixture of the three in water. Metal concentrations were analyzed using a Prodigy Dual View Inductively Coupled Plasma Spectrophotometer using a nitric acid microwave digestion assay with detection limits of 2.16 ppb, 1.56 ppb, and 4.32 ppb for Cu^{2+}, Zn^{2+}, and Pb^{2+}, respectively. Note: One of the Cu^{2+} samples exposed to Osorb_A media was found to have a copper concentration higher than the initial sample, and was thus determined that the sample was compromised and was excluded from analysis based on statistical evaluation of the data set.

Osorb Media Sample	**Capture of Cu^{2+}**			**Capture of Zn^{2+}**			**Capture of Pb^{2+}**		
	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture
_A	40.5	*133.2*	--	44.8	10.5	76.6	27.5	4.0	85.5
	40.1	5.9	85.3	43.4	12.5	71.2	27.0	4.0	85.2
	40.6	2.0	95.1	44.4	9.5	78.6	27.5	4.0	85.5
_B	40.5	2.0	95.1	44.8	11.7	73.9	27.5	4.0	85.5
	40.1	2.0	95.0	43.4	16.2	62.7	27.0	4.0	85.2
	40.6	2.0	95.1	44.4	10.2	77.0	27.5	4.0	85.5
_C	40.5	2.0	95.1	44.8	12.6	71.9	27.5	4.0	85.5
	40.1	3.4	91.5	43.4	11.0	74.7	27.0	4.0	85.2
	40.6	2.8	93.1	44.4	11.6	73.9	27.5	4.0	85.5

Osorb Media Sample	**Capture of Cu^{2+}**			**Capture of Zn^{2+}**			**Capture of Pb^{2+}**		
	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture	Initial Conc. (ppm)	Post Osorb Exposure (ppm)	% Capture
_A	39.6	2.0	94.9	45.2	9.9	78.1	32.1	4.0	87.5
	40.2	2.0	95.0	46.2	13.5	79.8	29.8	4.0	86.6
	42.1	2.6	93.8	47.9	13.6	71.6	30.7	4.0	87.0
_B	39.6	2.0	94.6	45.2	14.0	69.0	32.1	4.0	87.5
	40.2	2.0	95.0	46.2	9.9	78.6	29.8	4.0	86.6
	42.1	2.0	95.2	47.9	8.3	82.7	30.7	4.0	87.0
_C	39.6	4.2	89.4	45.2	11.5	74.6	32.1	4.0	87.5
	40.2	2.6	93.5	46.2	9.8	78.8	29.8	4.0	86.6
	42.1	3.8	91.0	47.9	11.6	75.8	30.7	4.0	87.0

Table A-2. Raw data to determine percent reduction of a mixture of munitions and dissolved metals using different ratios of Osorb media to thiolated media to determine the optimal formulation for the removal of both suites of contaminants of interest. Capture of munitions was calculated by reduction in HPLC peak area of samples exposed to Osorb media relative to a control. Capture of dissolved metal ions determined by quantification of metals in aqueous solution as determined by ICP-AES after digestion post exposure to Osorb media relative to a control. Testing was completed in triplicate.

Sample Osorb media: Thiolated media	**HPLC Peak Areas**		**Concentration of Metal Ion (ug/mL)**		
	RDX	**TNT**	**Cu^{2+}**	**Zn^{2+}**	**Pb^{2+}**
Control (no Osorb media)	24.40	70.02	0.190	0.065	0.015
	24.07	68.64	0.188	0.062	0.016
	24.33	71.68	0.160	0.061	0.014
100:0	9.92	8.56	0.100	0.023	0.012
	10.32	9.64	0.094	0.020	0.008
	9.29	8.03	0.059	0.016	0.006
0:100	8.01	6.28	0.042	0.016	0.004
	9.10	9.45	0.030	0.018	0.004
	8.99	7.21	0.020	0.012	0.004
75:25	7.91	8.82	0.016	0.013	0.004
	10.25	9.03	0.016	0.020	0.004
	8.14	9.23	0.011	0.018	0.004
50:50	10.26	9.44	0.016	0.010	0.004
	20.56	10.85	0.014	0.008	0.004
	8.71	13.66	0.007	0.012	0.004
25:75	10.78	16.59	0.060	0.024	0.004
	10.42	11.93	0.015	0.021	0.004
	10.27	15.24	0.014	0.019	0.004

Table A-3. Raw data of the adsorption of RDX, TNT, and dissolved metals from stirred and unstirred solutions. The dissolved metals were quantified using ICP-AES and are reported as ppb. The RDX and TNT were analyzed using HPLC-UV and are reported as peak areas. The % capture of each specie, as reported in Table 12, was determined by measuring the relative abundance of the munition or metal in the water containing a passive sampler relative to a control sample of the water. All samples were measured in triplicate.

Stirred samples					
Passive Sampler Deployment Time	Cu^{2+} (ppb)	Zn^{2+} (ppb)	Ni^{2+} (ppb)	RDX (peak area)	TNT (peak area)
0 min (Control)	26.2	46.9	17.5	355.4	62.1
	37.6	66.3	24.4	364.8	65.5
	31.5	49.1	18.8	363.2	61.7
30 min	27.0	37.8	14.4	359.2	59.3
	33.6	55.4	22.4	362.8	58.2
	26.8	65.5	17.6	357.9	56.4
1 hr	21.1	32.8	14.1	351.5	60.5
	31.4	52.5	22.1	353.3	56.9
	23.9	40.8	26.9	347.2	50.2
2 hr	17.2	29.9	12.7	344.4	56.3
	27.3	49.0	22.1	344.6	53.9
	19.5	32.6	14.9	330.3	48.3
4 hr	14.0	26.0	10.4	335.0	50.1
	22.8	50.3	20.7	334.6	50.0
	14.8	28.9	12.7	316.8	38.8
8 hr	10.9	26.6	9.3	327.6	39.6
	17.4	45.0	20.8	319.6	41.9
	13.3	28.9	11.8	311.2	35.5
24 hr	3.5	17.7	6.8	311.8	29.8
	11.7	45.8	21.7	297.4	23.0
	11.5	29.5	11.2	314.9	37.0
Unstirred samples					
Passive Sampler Deployment Time	Cu^{2+} (ppb)	Zn^{2+} (ppb)	Ni^{2+} (ppb)	RDX (peak area)	TNT (peak area)
0 min (Control)	35.5	51.5	24.6	341.4	62.0
	37.7	81.2	25.6	362.5	64.3
	38.6	57.4	27.5	347.9	58.0
1 day	23.8	42.9	19.9	344.4	68.0
	24.2	42.3	19.1	360.2	62.0
	26.4	43.7	18.8	359.8	57.7
3 days	18.7	35.8	15.2	339.0	58.3
	18.6	45.7	14.5	351.9	59.2
	21.2	38.6	15.5	355.2	55.8
6 days	14.7	29.6	11.7	317.7	53.8
	14.4	28.5	9.9	351.9	55.5
	17.5	32.5	12.4	349.2	54.0
7 days	13.9	30.2	11.1	334.7	56.6
	14.3	29.3	10.0	347.2	53.3
	16.6	30.9	11.3	349.4	55.8
10 days	14.5	27.3	11.3	327.9	47.6
	11.8	24.5	9.1	347.9	48.8
	15.0	27.1	9.9	347.0	49.7
14 days	9.2	20.1	8.4	325.6	34.4
	10.1	21.1	7.4	342.1	39.7
	12.4	27.2	9.2	342.5	41.7

Table A-4: Passive sampler response for RDX in both seawater and deionized water as a function of solution phase concentration. Passive sampler response measured via HPLC analysis of extracts of the samplers using a calibration curve for quantification. All samples were done in triplicate. The theoretical concentration for the extracts out of a 1.9, 7.5, and 50 ppb solution were 3325, 13 125, and 87 500 ppb, respectively. Data can be found in Figures 11 and 12.

Solution Phase Concentration (ppb)	**Passive Sampler Response**	
	Seawater (ppb)	**Deionized Water (ppb)**
1.9	404	323
	442	0
	543	0
7.5	1048	1541
	605	504
	1541	524
50.0	12573	3135
	5041	4653
	8925	5305

Table A-5: Passive sampler response for Zn^{2+} in both seawater and deionized water as a function of solution phase concentration. Passive sampler response measured via ICP-AES analysis of extracts of the samplers. All samples were done in triplicate. Data can be found in Figures 13 and 14.

Solution Phase Concentration (ppb)	**Passive Sampler Response**	
	Seawater (ppb)	**Deionized Water (ppb)**
0.2	549.5	247.7
	471.6	330.4
	338.4	249.0
0.8	345.5	253.7
	502.2	233.3
	358.4	243.2
1.9	357.9	195.2
	392.1	189.5
	542.9	200.2
7.6	639.0	193.2
	496.6	300.1
	924.2	193.1
50.0	2 453.1	297.5
	954.7	384.5
	789.7	269.2

Table A-6. The concentration of RDX and TNT in the sampler extract relative to the applied concentration of each munition. Samplers were tested in triplicate.

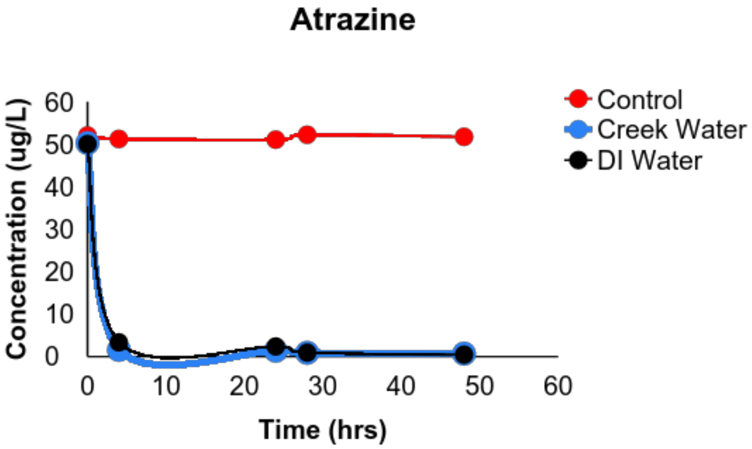
Applied Concentration (ppb)	Sampler Extract Concentration	
	RDX (ppb)	TNT (ppb)
10	58.0	198.3
	56.9	194.6
	41.9	142.9
25	60.3	206.2
	90.9	311.0
	106.8	365.3
50	177.5	607.1
	260.1	889.9
	129.4	442.7
100	353.5	1209.3
	203.5	696.0
	474.2	1622.0
250	1216.0	4159.5
	736.5	2519.2

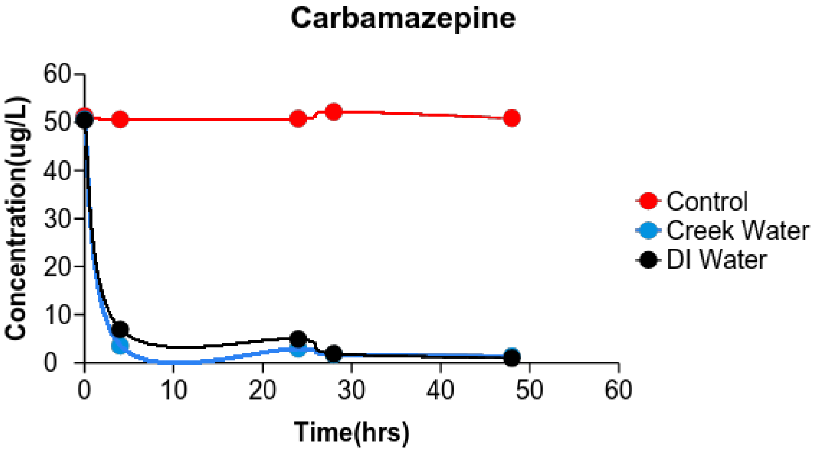
Table A-7. The mass of munitions in Osorb media extracted from the passive samplers as a function of flume flow rate. All data collected in triplicate and averaged. The concentration of the munitions in the water sample is also reported.

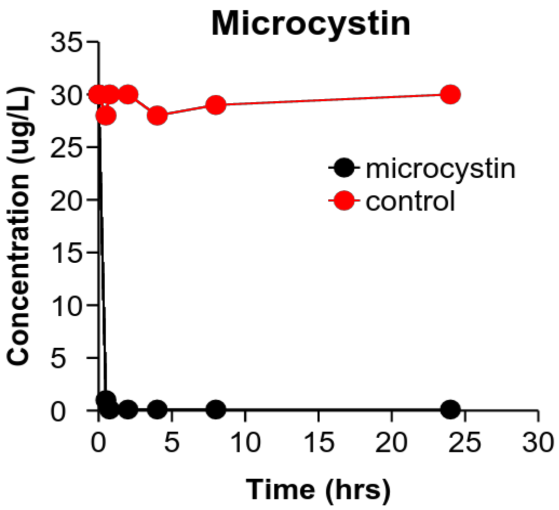
Flume Flow Rate (cm/sec)	Amount of Munitions in Osorb Media (ng)			
	2,6-DNT	2,4-DNT	TNT	RDX
7	822 ± 231	758 ± 74	236 ± 105	32 ± 1
15	7819 ± 1019	7652 ± 1709	5216 ± 701	777 ± 374
30	9773 ± 2085	10496 ± 1919	8216 ± 1471	3208 ± 1800
Munitions in Water (ng/L):	705	655	359	856

Appendix B: Supporting Data

Other Adsorption Data from batch equilibrium studies

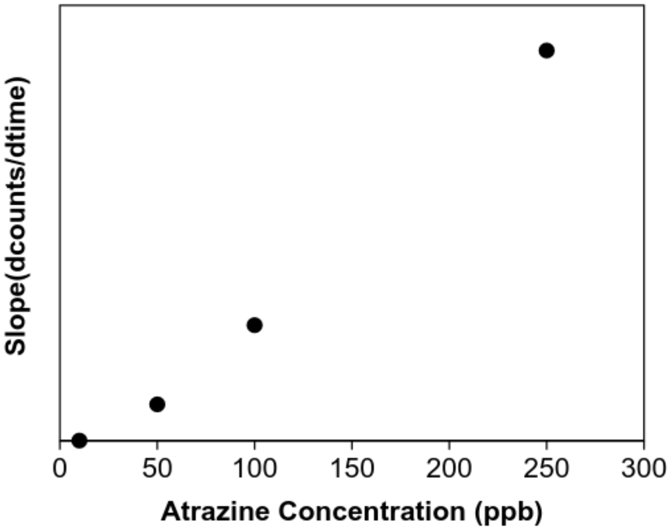






Other continuous flow data

Rate of atrazine uptake as a function of concentration – supports linear response to aqueous phase concentration.



Appendix C – Publications and Conferences

Peer review publication (accepted)

Shane A. Morrison, Jason B. Belden, Calibration of nylon organic chemical integrative samplers and Sentinel samplers for quantitative measurement of pulsed aquatic exposures, *Journal of Chromatography A*, Available online 26 April 2016, ISSN 0021-9673, http://dx.doi.org/10.1016/j.chroma.2016.04.072.

Conference Presentations

Paul L. Edmiston. Society of Environmental Toxicology and Chemistry Meeting, "Multi-Analyte Passive Samplers with Tissue Mimicry to Measure the Bioavailability of Contaminants", Salt Lake City, Utah October 2015

Evaluation of a new type of biomimic passive sampler for water and sediment sampling is being evaluated as part of SERDP project ER-2541. The sampler is based on porous-elastic organosilica sorbents which are swollen with triolein to mimic the tissues of benthic organisms. The media is designed to simultaneously measure both organic and metal ion contaminants in water and sediment. Interior surfaces of organosilica matrix are functionalized with thiol groups to mimic the metal ion binding proteins found in biological systems. Adsorbed organic contaminants can be recovered by solvent rinse whereas the metals are subsequently desorbed via acid rinse. In this manner, the sampler media mimics fish tissue, but is molecularly engineered to be non-degradable and robust. The sampler can be loaded with organic and inorganic performance reference compounds for improved quantitation. The purpose of the samplers to determine bioaccessibility of contaminants by depleting both the reversibly bound fraction (*C*rev) and freely dissolved pools (*C*free) as would occur on an organismal level. Simultaneous measurement of both *C*free and *C*rev allows for measurement of bioaccessibility without significant use of modeling. Within a regulatory context, this can allow decisions to made on the extent of accessible contaminant loads instead of relying *C*total. Since *C*total may drastically overestimate environmental impact, such data may likely improved decision making capabilities. Samplers have been tested for the simultaneous measurement PCBs, dioxins, RDX, TNT, Cu^{2+}, Zn^{2+}, and Pb^{2+}.