

FINAL REPORT

Optimization of Integrative Passive Sampling Approaches for Use in the Epibenthic Environment

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14. ABSTRACT The overall objective of this research was to develop an integrative passive sampler (IPS) design and protocol that accurately integrates time-weighted concentrations of munitions constituents (MCs) in aquatic systems regardless of the magnitude of flow. Investigations focused on further development of the Polar Organic Chemical Integrative Sampler (POCIS) including modification of sampler design, addition of a performance reference compound (PRC), and development of a microsensor for flow that can be co-deployed. Addition of flow disrupting screen reduced the impact of flow and could be developed pending further research and optimization. PRCs were found to be helpful for some, but not all analytes. Finally, a promising flow sensor was developed. Although all three approaches had relatively positive outcomes, the microsensor for flow had the best opportunities for technology transfer and is suggested for future development.					
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List of Acronyms

ADNT	Aminodinitrotoluene
ADV	Acoustic Doppler Velocimeter
DANT	Diaminonitrotoluene
DEA	Deethyatraine
DNT	Dinitrotoluene
DoD	Department of Defense
ERDC	U.S. Army Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
GC/MS	Gas Chromatography/Mass Spectrometry
HLB	Hydrophilic-lipophilic balance (POCIS sorbent)
IPS	Integrative Passive Sampler
Kow	Octanol-water partition coefficient
MEC	Munitions and Explosives of Concern
MC	Munition constituents
MMRP	Military Munitions Response Program
NAVFAC	Naval Facilities Engineering Command
NESDI	Navy Environmental Sustainability Development to Integration
OSU	Oklahoma State University
PES	Polyethersulfone
POCIS	Polar Organic Chemical Integrative Sampler
PRC	Performance Reference Compound
PSD	Passive Sampling Device
RDX	Hexahydro-1,3,5-trinitro-s-triazine (also Royal Demolition Explosive)
Rs	Sampling Rate
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SPAWAR	Space and Naval Warfare
SPE	Solid phase extraction
SSC-PAC	SPAWAR Systems Center Pacific
TNT	Trinitrotoluene
TWA	Time-weighted average
USACE	United States Army Corps of Engineers
USB	Universal Serial Bus
USEPA	United States Environmental Protection Agency
USN	United States Navy
UXO	Unexploded ordnance
UWMM	Underwater Military Munitions

Keywords

Munition constituents, TNT, RDX, Unexploded ordnance, Passive sampler, POCIS, Integrative, Sediment, Benthic

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Abstract

Objective: The overall objective of this research is to develop an integrative passive sampler (IPS) design and protocol that accurately integrates time-weighted concentrations of munitions constituents (MCs) within water from epibenthic environments. Although integrative passive sampling has been demonstrated as a promising technique for MCs, current sampler designs and technology do not account for variations in sampling rate due to changes in flow and turbulence near the sampler. In complex environments at the sediment – water interface, this may limit the utility of passive sampling. Thus, our specific objectives are targeted at three different approaches to improve calibration of samplers including: 1) test options for optimization of passive sampler design to reduce boundary limitations and make sampling rates more uniform across environmental conditions; 2) modify and incorporate sensors for measurement of in-situ flow and temperature to correlate environmental conditions with lab calibrations; 3) test potential performance reference compounds to measure in-situ sampling kinetics allowing adjustments of sampling rates. Following improvement of measurements during varying flow, further testing could proceed in follow-on studies to test validity of the samplers in the epibenthic environment for measuring exposure to benthic and epibenthic organisms.

Technical Approach: Our study was divided into three tasks, each investigating an approach for improving the accuracy of sampling rates of IPS across changes in flow and turbulence.

In Task 1, we investigated whether modifications to IPS design can decrease flow dependency of sampling rate. We compared existing POCIS samplers, a design with demonstrated utility but susceptibility to flow variations, with two additional configurations that we hypothesized would limit dependency of flow on sampling rate. Tested configurations included thickening the membranes of the sampler and placing a nylon screen 8mm from the membrane. Calibration studies of these design configurations were conducted using high and low flow conditions. Criteria for a successful sampling design was to have minimum differences in sampling rate between flows, yet high enough sampling rates to prevent loss of method sensitivity.

In Task 2, we investigated the use of performance reference compounds (PRCs) to adjust IPS calibration in-situ allowing more accurate prediction of water concentrations during fluctuating flow conditions. POCIS samplers were manufactured containing PRCs including ¹³C-caffeine. Calibration studies were conducted under static and flow conditions. The relationship of dissipation of the PRCs from the IPS and uptake of MCs were evaluated to determine if these compounds are acceptable as PRCs.

In Task 3, we investigated the potential for fitting an IPS with a microelectronic flow device. If flow is known, IPS calibration can be adjusted based on a series of calibration studies. A sensor was identified and tested for its potential in measuring flow on IPS both exposed directly to the external environment, and within deployment canisters typically used to protect IPS membranes from the harsh field environment. In addition, temperature sensitivity was determined and waterproofing techniques were investigated.

Results: In Task 1, doubling the sampler membrane did not greatly reduce the impact of flow on sampling rate. However, the addition of the nylon screen did greatly reduce the impact of flow on sampling rate. Changes in sampling rate between static and high flow were between 200-500% in traditional POCIS depending on analyte. With the screen in place changes due to flow

were less than 40%. Sampling rates were reduced with the addition of the nylon screen, but not enough to greatly impact sensitivity. Placement of a nylon screen over the sampler requires limited technology improvement and it can be placed over commercially available samplers allowing rapid technology transfer.

In Task 2, PRCs resulted in improved calibration across flows for most analytes; however, a few important analytes such as RDX were not improved. For TNT and other nitrotoluenes, corrected sampling rates were 73-122% between flow conditions. However, for RDX, sampling rates varied by 191-206%, resulting in a similar error potential that existed due to flow rate without using a PRC. Despite some promise, technology transfer for the PRC approach will not be easy. The commercial provider appears to be reluctant to include a PRC as there is not a consensus choice of PRC and the best PRC is likely analyte specific. Addition of compounds to the sampler would likely be a custom process. Moreover, the PRC approach will require additional analyses cost, as most PRCs will not be on the target analyte list.

In Task 3, an electronic sensor that is sensitive to water flow was identified, successfully water-proofed, and calibrated. The influence of temperature was described and can be easily adjusted. The device is highly sensitive across low flow conditions, which matches the flow rates that are most impactful to POCIS sampling rates. The device was successfully deployed inside and outside of a POCIS deployment canister demonstrating that a small device can be deployed near the membrane inside the canister. Moreover, there were flow differences observed between the inside and outside of the deployment canister demonstrating that an internal device is necessary. The device could be broadly applicable to numerous aquatic studies even beyond passive sampling. Thus, we expect interest in commercial technology transfer.

In conclusion, the addition of a nylon screen over commercially-available samplers and placement of a flow sensor were found to be promising approaches to reduce the impact of flow on IPS sampling rates. With minimal further development, these approaches will be ready to test in mesocosm and field studies within the epibenthic environment. In these studies, we will be able to further optimize sampling approaches for UXO sites.

Benefits: The improved ability to accurately sample and quantify concentrations of MCs, and other moderately polar organic contaminants, in the epibenthic environment provides a valuable tool for monitoring potential low-level and/or episodic releases at unexploded ordnance (UXO) or discarded military munitions (DMM) sites, thus enhancing existing capabilities with POCIS for the water column. It is anticipated that the possibility of employing the highly promising POCIS technology to multiple environments, including open water and epibenthic zones in fresh and salt water, will provide more options to DoD end users associated with the Military Munitions Response Program (MMRP). Thus, decision-making will be improved with respect to potential concerns regarding the need for removal or other costly remedial actions. For example, if detection of buried and leaking UXO is possible through epibenthic measurements, sampling and analysis of sediment and pore-water with unknown UXO sources can be minimized.

Objectives

The overall objective of this research is to develop an integrative passive sampler (IPS) design and protocol that accurately integrates time-weighted concentrations of munitions constituents (MCs) within water from epibenthic environments. Although integrative passive samplers have been demonstrated as a promising technique for MCs, current sampler designs and technology inadequately account for variations in sampling rate due to changes in flow and turbulences near the sampler. Thus, our specific objectives were targeted at three different approaches to improve calibration of samplers including: 1) test options for optimization of passive sampler design to reduce boundary limitations and make sampling rates more uniform across environmental conditions; 2) test potential performance reference compounds to measure in-situ sampling kinetics allowing adjustments of sampling rates; and 3) modify and incorporate sensors for measurement of in-situ flow and temperature to correlate environmental conditions with laboratory calibrations. By testing multiple approaches, we were able to identify promising approaches for future development and use. Moreover, improvement of the integrative passive sampling approach leads to better ability to use the sampler in an epibenthic environment. Due to the frequent positioning of unexploded ordnance (UXO) in sediment and relatively hydrophilic nature of MCs, we posit that this sediment-seawater interfacial environment is important both as an area of likely exposure to organisms and the optimal location for screening-level evaluation of environmentally relevant MCs at potentially contaminated sites.

Background

The Department of Defense (DoD) has custody and responsibility for human safety and environmental stewardship for coastal ranges, many of which have underwater sites that are known to contain underwater military munitions (UWMM) such as UXO as a result of historic military activities. In addition to munitions and explosives of concern (MEC) blast (safety) considerations, regulators are increasingly concerned about potential ecological impacts of munitions constituents such as RDX and TNT on the marine environment, which has resulted in costly risk assessments (e.g., NAVFAC 2009, USACE 2012) and could lead to potentially unnecessary remediation efforts. Although UWMM have the potential to corrode, breach, and leak munitions constituents (including TNT, RDX, and their major degradation products) into aquatic environments (Li et al. 2016, Lewis et al. 2009; Pascoe et al. 2010; Rosen and Lotufo 2010; Wang et al 2011), a number of challenges prevent accurate assessment of environmental exposure using traditional water, sediment, and tissue sampling and analyses. These challenges include a high level of effort required to measure MC release during episodic events or at extremely low-levels, identify leaking UXOs, determine the nature of the leakage, e.g., varying levels of corrosion (Li et al. 2016), low dissolution rates (Lynch et al. 2002) attenuated by biofouling, biodegradation, photolysis, and hydrolysis (Numerous chapters in Chappell, Price, and George. 2011), and low bioaccumulation potential (Lotufo et al. 2009; Lotufo et al. 2013).

Release of MCs is expected to be in the epibenthic environment, i.e. at or near the sediment/water column interface, due to spatial location of ordnance on the sea floor. Upon release, MCs can dissolve and diffuse into the water column or sorb into sediment (Rosen and Lotufo 2010, Lotufo et al. 2013). Within biologically active sediment, many MCs are rapidly degraded (Lotufo et al. 2013). In the upper water column, especially in marine systems, the large volume of water can ultimately result in dilution below any potential effective concentrations.

Thus, the epibenthic environment is the most likely site for an ecological effect to occur and should be a high priority for environmental monitoring. Many organisms that are considered benthic, including most crustaceans and mollusks, are primarily exposed to water in the epibenthic environment in contrast to pore-water within sediment. Moreover, measurement in the epibenthic environment provides an opportunity to sample more broadly across a potentially heterogeneous exposure environment. Given the limited magnitude of partitioning to sediment from water and the high sensitivity of the passive sampling approach, it is likely that measurement of epibenthic water using integrative sampling is sensitive enough to screen for pore-water contamination.

Due to the short-half life, and potential for fluctuating release with low residence times, concentrations of MCs are likely to be variable at UXO sites. Standard environmental sampling, such as grab sampling of surface water or collection of sediment, may inadequately capture pulsed concentrations that may occur or provide an environmentally relevant measure of dose. Similarly, passive sampling devices using an equilibrium approach will likely inaccurately describe a pulse of material as the system is not in equilibrium and if the sample is collected during low environmental concentrations, estimated water concentrations would be biased low. Devices designed for hydrophobic contaminants, such as PAHs and PCBs, typically will not efficiently sample weakly hydrophobic compounds such as MCs to allow for part per trillion (ppt) level detection. Solid phase micro extraction fibers (SPME) have been used in sediment for numerous compounds and have the theoretical advantage of measuring pore-water concentration in sediment (Conder et al. 2003). However, reporting limits can be a challenge as the amount of material sampled per length is minimal, and insertion of great lengths into sediment can be problematic in the field (NESDI Project #465; Lotufo et al., in prep). SPME fibers can be used for MCs, and although the technique showed some promise (Conder et al. 2013, Lotufo et al., in prep), detectability was an issue at low water concentration. Also, relevant fiber options proved to be more fragile than desired for field use.

In contrast, our team of researchers (including PI Belden and co-PIs Rosen, Lotufo, and George) recently demonstrated that integrative passive sampling provides an opportunity to sample MCs and obtain time-weighted water concentrations and very low detection limits in water (NESDI Project #465 and ESTCP Project #ER-201433). Our previous and ongoing work has focused on measuring explosives in open water. We have demonstrated that commercially available POCIS have effectively linear uptake for at least 28 days for many MCs and are highly integrative (Figure 1, Belden et al. 2015).

In order for integrative samplers to accurately predict time weighted water concentrations (C_w) described in Eqn. 1, they are empirically calibrated during laboratory studies (Morin et al. 2012; Harman et al. 2012).

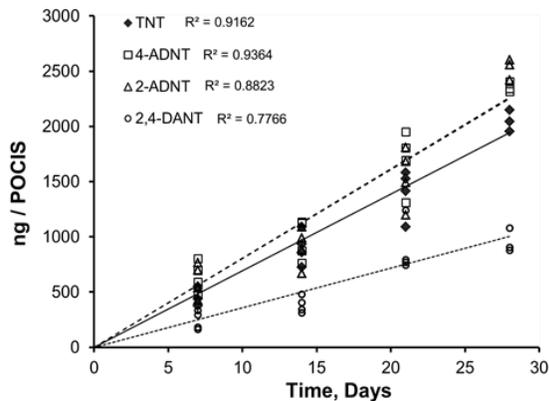


Figure 1. Accumulation of TNT and metabolites in POCIS demonstrating linear uptake for 28 days (Belden et al. 2015)

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

In this equation, N is the mass of the chemical accumulated by the sampler (typically in ng), R_s is the sampling rate (L/day), and t is the exposure time (days). For our previous studies with POCIS, laboratory controlled sampling rates were used to calculate C_w based on MC concentration found within the sampler. POCIS with high sampling rates for MCs allowed measurement of water concentration of less than 50 ng/L (ppt).

Environmental conditions such as flow rate, salinity, temperature, and biofouling can all cause variations in the sampling rate. However, the potential bias for temperature and salinity is typically low as long as calibration studies are conducted under conditions similar to expected field conditions. Temperature within normal environmental range (5-25° C) have been reported to result in lower than two-fold change in R_s (Li et al. 2010; Harman et al. 2012). Salinity can typically be predicted based on expected environmental usage and POCIS are relatively resistant to biofouling within the water column (Harman et al. 2012). Biofouling is more of a concern in longer studies. Previous work by our group (ESTCP Project #ER-201433) has demonstrated little effect of biofouling on sampling rates for 14d deployments despite visible fouling. Thus, POCIS can be used in marine and freshwater environments.

In the epibenthic environment, however, utilizing IPS may be more challenging, as flow may be limited or variable due to bottom currents and the presence of biofouling, which may occur more readily. These factors could reduce the accuracy of TWC quantitation, as sampling rates would be variable. For example, sampling rate studies comparing static flow to mixing conditions has increased sampling rates as much as 5-9x depending on the analyte and study (Harman et al. 2012). POCIS samplers, which are the best IPS tested for MCs, are optimized to have high uptake rates and thus tend to be more flow-dependent on loading rate, but have been observed to be resistant to biofouling especially within a protective cage (unpublished results, NESDI Project #465, Rosen et al.). Thus, our focus will be targeted towards approaches that reduce the effect of varying flow on sampling rate.

Harman et al. (2012) suggested several approaches that could be useful to improve calibration of POCIS-style samplers. These included: 1) adjust sampler design to reduce the impact of low and fluctuating flow on uptake; 2) developing a protocol for using performance reference compounds (PRC); and 3) utilizing passive flow monitors (O'Brian et al 2011). Each of these approaches has potential, yet is not reliable at the present state of development.

Sampler design modification.

The sampler design could be adjusted to reduce the impact of low and fluctuating flow on uptake. If uptake is the same across flows, then knowledge and adjustment of R_s across flows is not necessary. A single static calibration would be required reducing the expenses and effort require to calculate accurate sampling rates. Two processes primarily regulate uptake of an integrative sampler; 1) permeation through the sampler membrane; and 2) diffusion through the aqueous boundary layer (ABL). It is the slower of these two processes that determine the sampling rate (Seethapathy et al 2008). Change in flow can change the size of the ABL resulting in varying diffusion distances. However, if the rate of permeation through the sampler membrane is significantly slow, it will become limiting despite changes occurring in the ABL. The result is an increase in stability of R_s despite changes in flow. Changing the permeation rate

has been successful in other types of samplers by using a thick ceramic enclosure (Bopp et al. 2005; Cristale et al. 2013) or adding a diffusion gel similar to the DGT design for metals analysis into a POCIS-style design (o-DGT; Chen et al. 2013). However, these approaches require significant changes to the POCIS design that has already been demonstrated for MCs. Working within the POCIS design, it may also be possible to increase the thickness of the polyethersulfone membranes of POCIS samplers, or to add a secondary screen outside of the main sampler. In each case, the modification to the sampler would ideally not result in increased adsorption to the membrane or screen, but would rather create a zone that allows an ABL to develop with constant size despite changes in flow. A possible issue with this approach is that with decreased diffusion, the sampling rate will also decrease, potentially making very low reporting limits problematic.

Performance Reference Compounds.

Performance reference compounds (PRCs) can be spiked into passive samplers prior to deployment. If the dissipation kinetics of PRCs from the sampler corresponds to the uptake rate of analytes, then the PRC behavior can be used to estimate R_s in-situ. Thus, factors such as temperature and flow are compensated by the PRC (Harman et al. 2011; Harman et al. 2012; Liu et al. 2013). PRCs have been effective for equilibrium-based passive samplers as stable isotope forms of the analytes can be spiked and dissipation is in direct relationship with uptake. However, PRC values have proven problematic for POCIS (Harman et al. 2011; Harman et al. 2012; Liu et al. 2013). Stable isotopes of analytes of interest do not work well, as fugacity out (due to desorption) is minimal for this type of sampler due to its integrative design. Thus, reference compounds with higher fugacity are required and the relationship between loss of the compound and MCs is not yet known. A recent study has shown a promising approach using deethylatrazine (DEA), a common metabolite of the herbicide atrazine (Mazella et al. 2010). DEA improved calibration in varying conditions for atrazine and other herbicides. In our previous POCIS research (Belden, et al. 2015), we measured uptake of caffeine concurrent with MCs. The sampler did not integratively sample caffeine by design; the concentration of caffeine on the sampler was at equilibrium with water concentrations prior to 14 days. Based on the assumption of first order kinetics, the half-life of caffeine in the POCIS was 7 days. This demonstrates that caffeine has high enough fugacity from a POCIS sampler that it could be useful as a PRC. Half-life values of seven days indicates that a 14-21 day period would be sufficient for a large enough loss of caffeine to allow for adjustments in calibration. Ideally, loss would be greater than 50% and less than 90% to prevent small errors in analytical measurement from biasing the results.

Flow Monitors

Passive flow monitors, including dissolvable substances such as gypsum casts (CaSO_4), have been co-deployed with the samplers for using dissolution to provide a measure of water flow and contact, allowing in-situ modification of calibration rates (O'Brian et al 2011). However, the rate of dissolution of most salts such as gypsum can be variable, as they depend upon environmental factors such as pH, and may not completely account for factors associated with adsorption of organic contaminants. Given current advances in environmental sensing, electronic flow detectors are likely a better option. Small flow detectors can be placed within the

sampler to characterize the flow. Such detectors commonly measure temperature concurrently. This approach insures that flow and temperature would be well known for each sampler and accounted for during calibration. However, this approach requires modified calibration procedures and physical modification of samplers.

Commercially available wind sensors are a low-cost option for instrumenting a POCIS-type sampler. Due to the small form factor of these devices, they can be interfaced inside of a POCIS canister to measure the flow velocity in the direct vicinity of the POCIS membrane. As an example, Wind Sensor Rev. C, made by Modern Devices (Providence, RI), has a small form factor and works via constant temperature anemometry. As designed, air flows passed a heated resistor maintained at a constant temperature on the device, and the heat is convectively transferred to the air. In response to this convective heat transfer, which is a function of air flow velocity, the device provides more power to the resistor to maintain a constant temperature greater than that of the air. Thus, by monitoring the power required to maintain a constant temperature, the wind velocity can be measured. In principle, these wind sensors can be converted to measure the flow velocity of water by modifying them with a thin waterproof coating. A proof of concept for integrating these sensors with POCIS-type samplers will require the calibration of the sensors with respect to flow velocity and temperature, and also will require interfacing the sensor inside of a POCIS canister and measuring the flow velocity within.

Materials and Methods

Optimization of Passive Integrative Sampler Design to Reduce Flow Dependency

Basic Sampler Design. As previously discussed, we have demonstrated the utility of POCIS samplers for MCs in water (Belden et al. 2015, NESDI #465, ESTCP #ER-201433). Therefore, POCIS was used as our starting design and our reference for new designs. POCIS were built to match the commercially available design consisting of two stainless steel rings (interior diameter 54 mm allowing surface area of 46 cm²). These rings compress two polyethersulfone (PES) microporous membranes (0.1 μm pore size Sterlitech, Kent, WA) with 200 mg of Oasis HLB adsorbent (Waters, Milford NH). Assembly is illustrated in Figure 2. Two variations were also tested. In order to test the effect of membrane thickness, samplers were built with double PES membranes. In order to test the impact of reducing direct flow across the membrane, nylon mesh screening (Nitex, 50μm openings; Pentair Aquatic Ecosystems) was placed at 8mm from the membrane on both sides by using additional stainless steel rings as spacers.

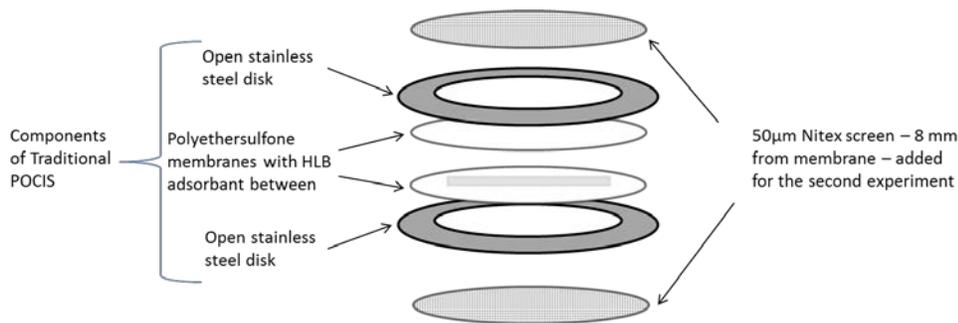


Figure 2. Illustration of a POCIS sampler in dismantled form. Two modifications to the sampler were tested including doubling of the polyethersulfone membrane and addition of nylon screen.

Passive Sampler Exposure. Passive samplers were exposed to analytes of interest using experimental units consisting of stainless steel pots (inner diameter: 40 cm, height: 30.5 cm) containing 30 L of tap water (Figure 3). To better achieve directional flow, smaller stainless steel pots (inner diameter: 15 cm, height 17.7 cm) were secured to an aluminum crossbar and suspended in the center of each unit. The bottoms were removed from the small pots, resulting in a stainless steel cylinder projecting into the upper portion of the water column. Flow was generated by securing aquarium pump heads (Aqueon Model AT10) to stainless steel threaded rods so that the pump head was 7.6 cm below the water surface and 3.8 cm above the bottom of the central cylindrical insert. Flow rate was determined for fast and slow flows by timing the movement of a float in replicate experimental units with mean (\pm standard deviation) of 9.33 (\pm 0.99) and 5.01 (\pm 0.49) cm/s, respectively. Experimental units with static flow were similarly constructed except the aquarium pump head was excluded. Each experimental unit contained three passive samplers (i.e. one sampler of each configuration). Nylon samplers were secured to stainless steel threaded rods horizontally in the water column with 3.1 cm of clearance between the top and the bottom sampler to ensure adequate and even flow across the nylon membranes.

Water was fortified with analytes using an acetone spiking solution (0.150 ml) to obtain 200 ng/L targeted water concentrations of MCs (trinitrotoluene, TNT; 4-aminodinitrotoluene, 4ADNT; 2-aminodinitrotoluene, 2ADNT; 2,6-dinitrotoluene, 26DNT; 1,3,5-trinitro-1,3,5-triazacyclohexane, RDX) and atrazine. Being a common target of analysis for agricultural systems, atrazine is the subject of a large collection of POCIS research. Because of the interest in this analyte, it was selected as a positive control to encourage commercialization of successful products. In order to maintain water concentrations, full static renewal occurred at 3.5 d intervals using secondary stainless steel pots so that samplers were out of the water for less than 5 seconds.

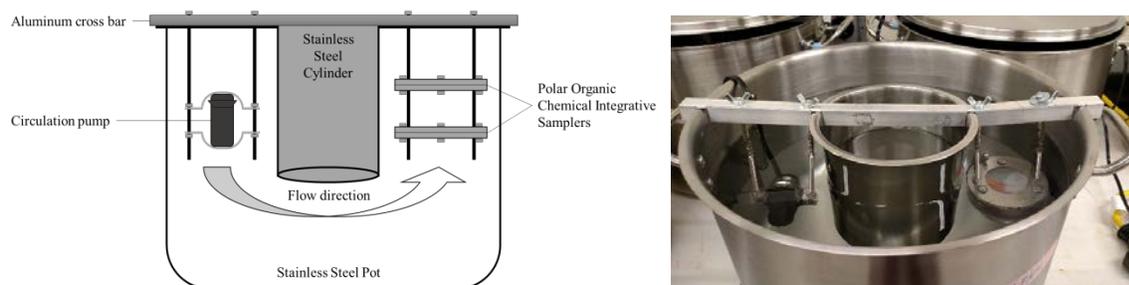


Figure 3. Left - Schematic of experimental unit with flow treatment. The circulation pump was omitted from static experimental units. To eliminate galvanic reactions within experimental units, all fastening/structural components exposed to water (i.e. pots, threaded bar, fastening nuts, washes, and clamps) were stainless steel. Right – photograph of system.

Experimental Design. Two separate experiments were conducted. In the first experiment, single and double membrane samplers were compared. Six chambers were established with flow (10cm/s) and six were static. Each chamber contained a single membrane and a double membrane POCIS. Three flowing and three static chambers were sampled at 7 d and 14 d (n=3 per treatment and time point). In the second experiment, traditional POCIS were compared against POCIS equipped with a nylon screen to reduce flow against the membrane. Six chambers were setup, each containing one traditional and one nylon screen sampler randomly assigned to top or bottom position. All samplers were collected at 14d (n=3 per treatment). After collection of POCIS, they were frozen until analysis. In both experiments, water samples

were collected before and after each renewal and at the beginning and end of each test using solid-phase extraction (SPE).

Analytical Measurements. Water was extracted utilizing HLB SPE cartridges (500mg, Waters). SPE cartridges were conditioned with 4 ml methanol, followed by 4 ml deionized water. Samples (500ml) were loaded onto the column at a rate of 15ml/min and air was then allowed to pass over the cartridge for 10 minutes to remove water. Cartridges were eluted with 10 ml ethyl acetate to recover analytes and the extract was evaporated to 0.5 ml prior to analysis. POCIS were extracted by removing membranes with a sharp utensil and rinsing all sorbent into an empty SPE cartridge with water. Water was vacuumed through to dry the sorbent, and the sorbent was eluted with 10 ml of ethyl acetate. Analysis was by GC/MS using GC methods described and optimized by Zhang et al. (2007) and EPA Method 8095 (USEPA 2007) and reported with use of mass spectrometry with 3-ion SIM analysis in Belden et al (2015). Internal calibration was performed using D5-TNT as the internal standard for all MC analytes. D10-atrazine was used for atrazine.

Statistical analysis

Sampling rates (R_s) were calculated for each POCIS based on Equation 1. Mean and standard deviations are presented. Two-way analysis of variance was conducted in SPSS to compare treatments ($p < 0.05$). A positive interaction suggested that the modification resulted in reduced differences in sampling rates.

Adjustment of R_s Using Performance Reference Compounds

Membrane samplers were built as described for the classical design in the previous experiment except that the HLB sorbent was fortified with PRCs, including caffeine- $^{13}\text{C}_3$, cotinine- d_3 , desisopropyl atrazine- d_5 (Santa Cruz Biotechnology, Dallas, TX), and fluoranthene- d_{10} (Accustandard, New Haven, CT). Targeted fortification levels were 1000 ng/ 200 mg HLB (thus 1000 ng/sampler). Modified methods proposed by Mazzella et al. (2008) were used for fortification. An aliquot (10 g) of HLB was weighed out in 200 mL French Square glass bottles, covered with 30 mL of methanol, and fortified with PRC stock solutions. Fortified bottles were placed on a rotating table and shaken at 125 rpm for 4 h to evenly distribute PRCs across the sorbents. Solvent was allowed to evaporate by removing the lids and shaken overnight (~12 h, 30 °C) at 125 rpm. Four 200 mg aliquots were immediately analyzed to determine PRC fortification levels and homogeneity.

Thirty POCIS were constructed. Three were frozen to provide an estimate of PRC recovered from a constructed sampler (time= 0). The 27 remaining were individually placed into exposure chambers as described in previous experiments and static renewal of the exposure water occurred every 48h. Decreased samplers and increased renewal prevented reuptake of PRCs. Each chamber was randomly assigned to one of three flows (static, low, high) and one of three time points (6, 12, 21d) resulting in three replicates at each flow-timing combination. Water samples and POCIS were recovered and treated as described for the previous experiment.

Performance reference compound (PRC) desorption can be used to correct laboratory calibrated R_s values. Assuming exchange kinetics are similar between PRCs and target analytes, the PRC elimination rate constant $k_{e\text{PRC}}$ can be derived using a first order elimination model

$$C_{\text{PRC}(t)} = C_{\text{PRC}0} \times \exp(-k_{e\text{PRClab}} \times t) \quad \text{Eqn. 2}$$

where $C_{\text{PRC}0}$ is the initial fortified PRC concentration (ng/g) and $C_{\text{PRC}(t)}$ is the remaining PRC concentration after an exposure of time (t) [20]. Similar to analyte R_s , PRC elimination is determined in controlled laboratory conditions ($k_{e\text{PRClab}}$). Rearrangement of Eqn. 2 allows for determination of PRC elimination during in situ ($k_{e\text{PRCinsitu}}$) deployments so that

$$k_{e\text{PRCinsitu}} = \frac{\ln(C_{\text{PRC}0}/C_{\text{PRC}(t)})}{t} \quad \text{Eqn. 3}$$

Once calibrated, $k_{e\text{PRClab}}$ can be used to normalize $k_{e\text{PRCinsitu}}$, thus providing a means to correct laboratory derived analyte sampling rates (R_{Scal}) resulting in-situ corrected sampling rates (R_{Scorr})

$$R_{\text{Scorr}} = R_{\text{Scal}} \times \left(\frac{k_{e\text{PRCinsitu}}}{k_{e\text{PRClab}}} \right) \quad \text{Eqn. 4}$$

In our test, we defined the “lab” rate as measured under static conditions and tested the correction factor approach by calculating R_{Scorr} for both flowing systems. R_{Scorr} was then compared to R_s measured in the flowing system.

Integration of Flow Sensors with POCIS

Sensor Modification and Operation. In order to monitor the flow with POCIS, modified constant temperature hot-wire anemometers were used. These flow sensors (Wind Sensor Rev. C) were acquired from Modern Devices, Providence, RI. In order to operate in an underwater environment while retaining sensitivity to flow, the sensors were modified by depositing a 10 to 20 μm thin conformal coating of Parylene-C using an SCS Labcoter 2 Parylene Deposition System located at the University of California San Diego (La Jolla, CA) Nano3 cleanroom facility. The Parylene-C coating provided an electrically insulating and water impermeable barrier which allowed the sensor to operate while submerged, and was formed thin enough to allow suitable heat exchange between the sensing element and the environment to monitor the flow velocity. The sensors were powered using a DC Power Supply set to 8 V. Two outputs (RV and TMP) of the sensor were monitored. The RV output is a voltage output that varies with fluid flow rate, and the TMP output is a voltage output that varies with temperature. Measurements of the sensor outputs were made using a programmed Arduino Uno microcontroller communicating serially via USB with a computer running data acquisition software in MATLAB. The microcontroller and data acquisition software enabled the concurrent collection and real-time monitoring of data for up to six channels, i.e. three sensors, and allowed the data to be written to a file for further analysis.

Calibration of Sensors. For current velocity studies, due to the importance of precisely controlling the hydrodynamic flow conditions, flow velocity calibration measurements of the sensors, as well as measurements comparing the flow inside and outside the POCIS canister, were conducted using a large 30,000 gallon flume located at the U.S. Army Engineer Research and Development Center (ERDC) in Vicksburg, MS. These measurements were performed at a constant temperature of 22 - 23 °C throughout.

Two sensors were calibrated with respect to flow velocity within the flume. They are designated as *Sensor 1* and *Sensor 2* throughout the report and were coated conformally with 20 μm and 10 μm of Parylene-C, respectively. In independent measurements, each sensor was interfaced on the exterior of a POCIS canister with the sensing element positioned away from the canister and perpendicular to the flow as depicted in Figure 4A. To constrain the POCIS canister orientation within the flume, the canister was tethered to the top, bottom, and sides of the flume as shown in Figure 4C. An acoustic Doppler velocimeter (ADV) (Nortek Vectrino) was used to quantify the average and standard deviation of the flow velocity within the flume under adjustable flow conditions ranging from an average of 5 to 25 cm/s. Measurements of the flow rate from the ADV were used as the reference to calibrate the RV output voltage of the sensor to a corresponding flow velocity. At each flow velocity, the RV output voltage of the sensor was acquired at a sampling rate of 10 Hz for a minimum of 5 minutes, and from this, the average and standard deviation were calculated. Measurements under static conditions were conducted in an unperturbed reservoir of water at the same temperature as the flume.

For calibration of the sensor with respect to temperature, a small, rudimentary flow apparatus comprised of a submersible pump, water reservoir, and adjustable channel was constructed at SSC-PAC where the flow velocity within a channel could be modulated by adjusting the cross sectional area of the channel. The RV output voltage of *Sensor 1* was measured continuously with respect to the TMP output voltage under static conditions and at three different flow configurations as the water reservoir was gradually heated. Using the flow velocity calibration of *Sensor 1* from the flume at the appropriate temperature, the flow velocity for the three additional configurations could be quantified as 11.7, 4.3, and 2.4 cm/s. The 0 cm/s flow rate measurements were attained by turning off the pump and waiting 2 minutes for the water to become static. For each TMP output voltage value and flow configuration, the average and standard deviation for the corresponding RV output voltage were calculated.

Monitoring Internal Flow within POCIS Canister. To monitor the internal flow within the POCIS canister, an individual sensor was interfaced to the inside wall of a POCIS canister as shown in Figure 4B such that the sensing element was perpendicular to the flow within the flume. Measurements of *Sensor 1* and *Sensor 2* internally interfaced to the POCIS were conducted in separate, independent measurements. The ADV was used to quantify the average and standard deviation of the flow velocity external to the POCIS canister over a range of external flow velocities from 5 to 25 cm/s. At each external flow velocity, the RV output voltage of the internally interfaced sensor was acquired at a sampling rate of 10 Hz for a minimum of 5 minutes, and from this, the average and standard deviation were calculated. By using the calibration of the RV output voltage versus flow velocity for each sensor, the flow velocity at the sensor location within the POCIS canister and the corresponding error bars were determined.

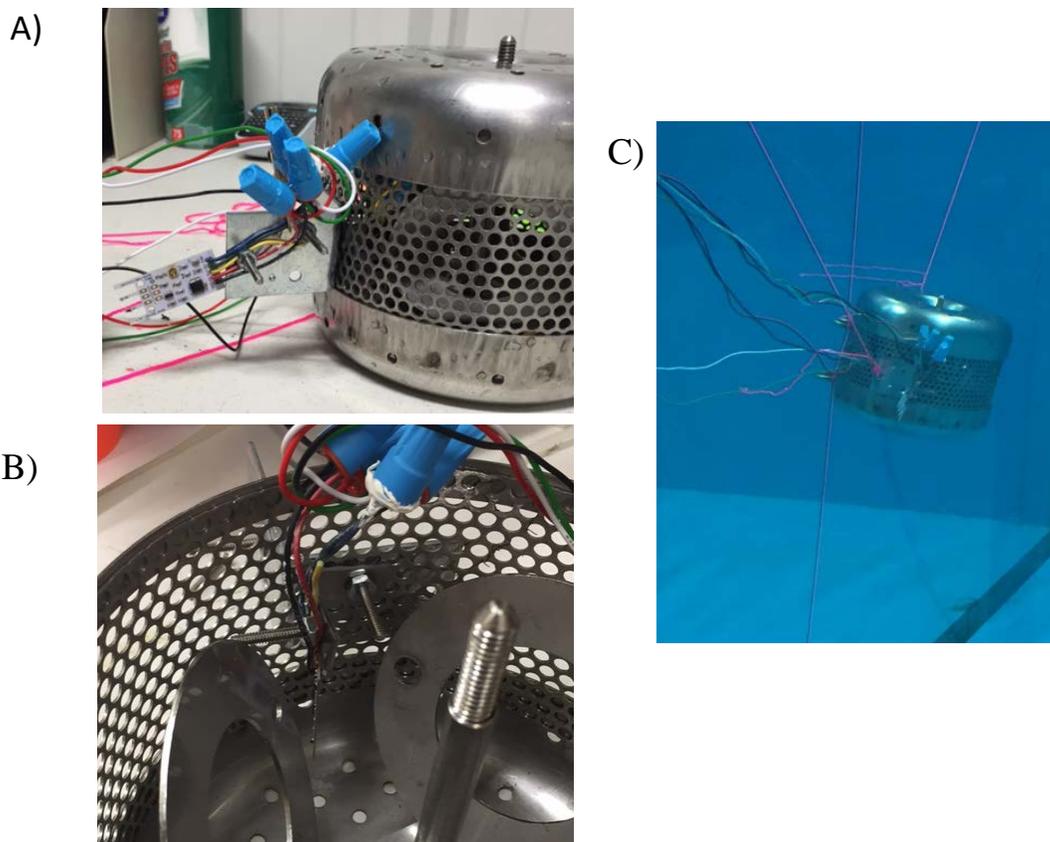


Figure 4. Sensor and POCIS canister calibration set-up. A) Sensor interfaced to outside of POCIS canister. B) Sensor interfaced to inside of POCIS Canister. C) POCIS canister and sensor tethered inside flume at ERDC.

Results and Discussion

Optimization of Passive Integrative Sampler Design to Reduce Flow Dependency

Sampling rates for POCIS with both single and double membranes significantly varied between flow rates with higher flow resulting in 2-5x higher sampling rates ($p < 0.05$; Figure 5, Table 1) in both configurations. Doubling the membrane did not significantly decrease the effect of flow as indicated by a significant interaction term, except for atrazine ($p < 0.05$). Even for atrazine, a 2x difference was still noted between flowing and static systems when using double membranes (Table 1). However, doubling the membrane significantly reduced sampling rates for all compounds ($p < 0.05$) except RDX, which was the most polar compound tested. With double membranes the sampling rate frequently dropped below 0.05 L/day, which was our *a priori* minimum acceptable sampling rate. Although this level was set arbitrarily, the low rates coupled with minimal or no improvement led us to conclude that this line of investigation is not worth pursuing. The PES membrane has some adsorption capability for many analytes, which likely caused the decrease in sampling rate.

In contrast, placement of a screen over the sampler did decrease the effect of flow on sampling rate. Sampling rates for POCIS traditionally deployed (without a screen) varied with flow causing 3-5x higher sampling rates as demonstrated in the previous experiment (Figure 6,

Table 2). However, the effect of flow was minimized to less than 2x higher and R_s was not significantly different between static and high flow when a nylon screen was attached over the sampler (Figure 6 and Table 2). These results are very promising and would be a relatively low-expense and low-tech solution. The primary challenge remaining is that 50 μ m nylon screen tends to hold an air bubble, thus effort is required to assemble the apparatus underwater or a lag effect is expected while the air diffuses out. Optimization of screen pore size is required to further develop the product and avoid assembly or lag issues, while maintaining the positive decrease in flow sensitivity.

Deployment with the screen did reduce the sampling rate as compared to static measurement without a screen (Table 2). Thus, calibration with the screen attached is likely necessary if highly quantitative data are required. However, the magnitude of reduction caused by adding the screen is less than the magnitude of change caused by differences in flow. The uncertainty could be decreased by using screens even if only static data from literature were available for sampling rates, versus using calibration data measured under the wrong flow regimes in traditionally deployed POCIS.

Flow effects found in this study tend to be greater than flow effects from previous MC sampling rate studies conducted by our group (Lotufo et al. (in prep), based on ESTCP Project #ER-201433). The difference may be due to the current study investigating extremes in flow ranging down to static. Much less difference in flow was present between 7-30 cm/s in the previous work using more accurate flow measurements in a long flume. Additionally, the chambers used to test flow were not as precise as the long flumes and underestimation of water movement across the sampler due to turbulence in the benchtop chambers was likely. In spite of this, results obtained with and without screens under identical conditions are valid measures of quantitative differences in performance.

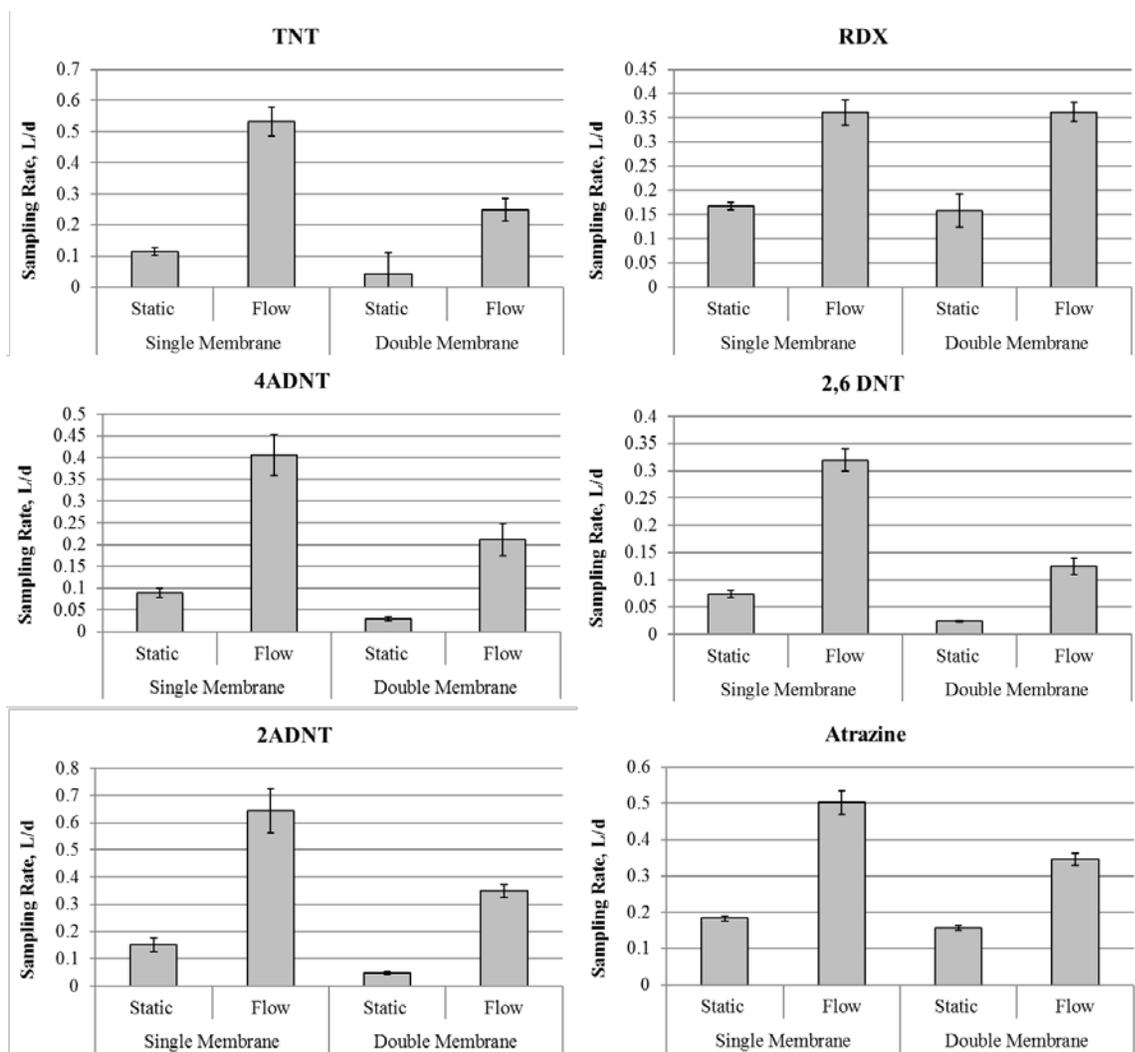


Figure 5. Sampling rates comparing POCIS with single (traditional) and double membranes under static and flowing (10 cm/s) conditions. Error bars represent standard deviation.

Table 1. Sampling rates for POCIS as compared to POCIS with a double membrane. % Change from Static compares the high flow sampling rate to the static sampling rate for the same sampler type to illustrate the impact of flow on that sampler design. R_s indicates sampling rate.

Analyte	Single Static	Single High Flow		Double Static	Double High Flow	
	R_s , L/d	R_s , L/d	% Change from Static	R_s , L/d	R_s , L/d	% Change from Static
TNT	0.114	0.532	467	0.042	0.248	590
RDX	0.168	0.361	215	0.158	0.362	229
4ADNT	0.088	0.406	461	0.029	0.211	720
2ADNT	0.151	0.644	426	0.048	0.350	729
26DNT	0.074	0.320	432	0.024	0.124	517
Atrazine	0.183	0.502	274	0.156	0.346	222

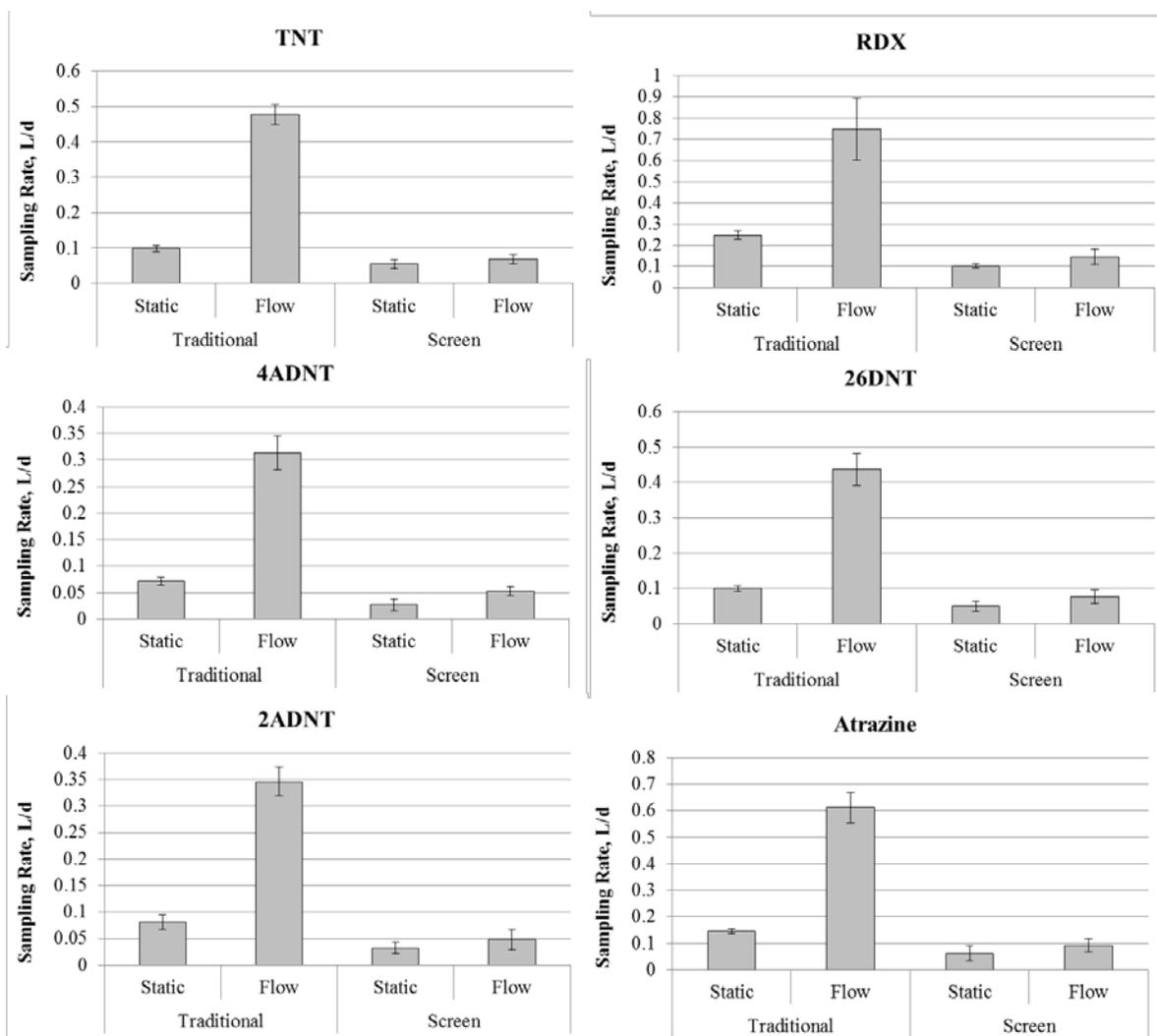


Figure 6. Sampling rates comparing POCIS with traditional deployment and with deployed with a 50 μ m nylon screen covering both membranes. Testing was done under static and flowing (10 cm/s) conditions. Error bars represent standard deviation.

Table 2. Sampling rates for POCIS as compared to POCIS with a nylon screen. % Change from Static compares the high flow sampling rate to the static sampling rate for the same sampler type to illustrate the impact of flow on that sampler design. R_s indicates sampling rate.

Analyte	Traditional			Screen		
	Static	High Flow	% Error	Static	High Flow	% Error
TNT	R_s , L/d	R_s , L/d	% Error	R_s , L/d	R_s , L/d	% Error
TNT	0.098	0.477	487	0.054	0.068	126
RDX	0.249	0.748	300	0.103	0.144	140
4ADNT	0.072	0.314	436	0.0275	0.0524	191
2ADNT	0.081	0.347	428	0.033	0.048	145
26DNT	0.099	0.438	442	0.049	0.076	155
Atrazine	0.147	0.613	417	0.062	0.091	147

Adjustment of R_s Using Performance Reference Compounds

Three PRCs, caffeine- $^{13}\text{C}_3$, cotinine- d_3 , desisopropyl atrazine- d_5 readily dissipated from the POCIS. However, cotinine- d_3 and desisopropyl atrazine- d_5 were eliminated relatively quickly with less than 5% remaining after 12 days in flowing systems resulting in concentrations that were quantitatively variable. Caffeine- $^{13}\text{C}_3$ dissipated at rates that allowed good measurement across time and flow conditions (Figure 7). Thus, we calculated PRC correct sampling rates using Caffeine- $^{13}\text{C}_3$. Fluoranthene- d_{10} , as expected, remained in the sampler always measuring within 20% of initial and no noticeable drop across time. The goal with this compound is to use it as a recovery control for quality control purposes.

Utilizing caffeine- $^{13}\text{C}_3$ as a PRC resulted in the ability to adjust for flow differences through PRC adjustment of the static sampling rate (R_{Scorr}) for almost every analyte resulting in more accurate estimates of water concentration (Figure 8). This is especially true for TNT and other nitrotoluenes that have similar properties. For these compounds, water concentrations estimated using R_{Scorr} were within 73-122% of the true water value (200 ng/L) even under flow conditions.

However, for RDX, R_{Scorr} was 191 and 206% of R_s for low and high flow conditions resulting in water concentrations that were skewed low. RDX has less change in sampling rate due to flow as compared to caffeine and nitrotoluenes leading to this error. In fact, for RDX the error resulting from using the PRC was as large as the error resulting from different sampling rates generated across flow rates. Although PRC corrections are likely effective for some compounds, they will not be effective for all analytes.

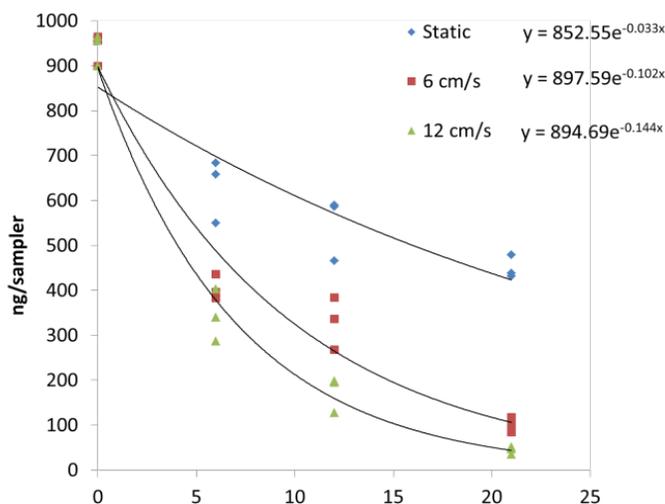


Figure 7. Elimination rate of RDX from POCIS across three flow rates.

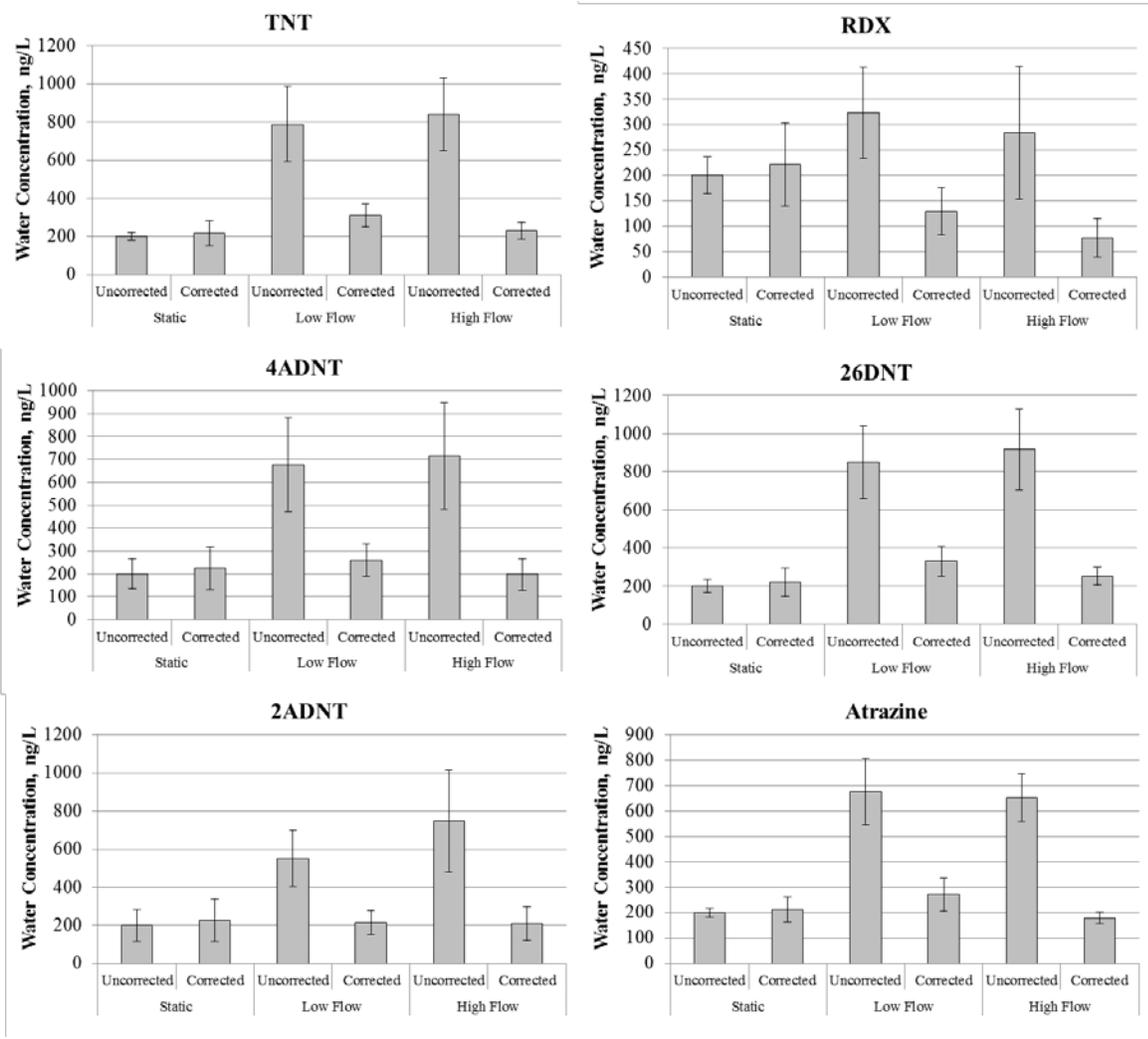


Figure 8. Water concentrations calculated across flow rates calculated using the static sampling rate and the static sampling rate using correction by a performance reference compound ($^{13}\text{C}_4$ -caffeine). Testing was done under static, low flow (5 cm/s), and moderate flow (10 cm/s) conditions. Error bars represent standard deviation.

Integration of Flow Sensors with POCIS

The RV output voltage calibration with respect to flow velocity for the sensors externally interfaced to the POCIS is shown Figure 9. These results demonstrate that sensors can be waterproofed and used to monitor the flow velocity of water. As seen from the curve fits, the RV output voltage for both sensors has an exponential dependence with respect to the flow velocity within measurement error. Because of this dependence, the sensors provide higher sensitivity over the low to mid flow velocities (0 to 10 cm/s) than at higher flow rates. It should be noted that the flow velocity within the flume (measured by the ADV) also showed variation, as indicated by the error bars, which may positively correlate to the variation of the RV output voltage. While outside the scope of these studies, maintaining a more uniform flow velocity field around the POCIS canisters would likely lead to greater calibration precision of the tested flow sensors.

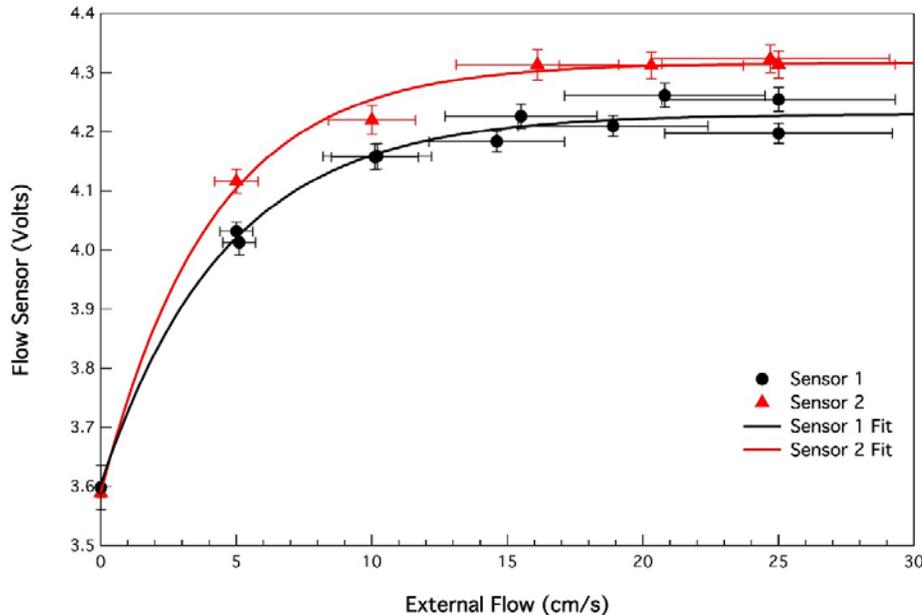


Figure 9. Calibration Curve for *Sensor 1* and *Sensor 2* positioned external to POCIS canister, perpendicular to flow within the ERDC Flume, and at $T = 22\text{-}23\text{ }^{\circ}\text{C}$. These data fit an exponential function within measurement error. Error bars represent standard deviation.

The temperature dependence of the flow sensors are shown in Figure 10 at four different flow velocities: 0, 2.4, 4.3, and 11.7 cm/s. For each configuration, including static flow, the data were fit to a linear curve. The slopes of the fits are plotted in Figure 11, where the slopes were observed to be consistent at each flow velocity. This supports using a single multiplicative correction factor to account for the effect of temperature on the sensor. The increasing size of the error bars in Figure 10 from the 11.7 to 2.4 cm/s configuration is likely due to a decreased uniformity in the flow field (increased variability in actual flow rate) due the rudimentary nature of the flow apparatus, as opposed to variability inherent to the sensor.

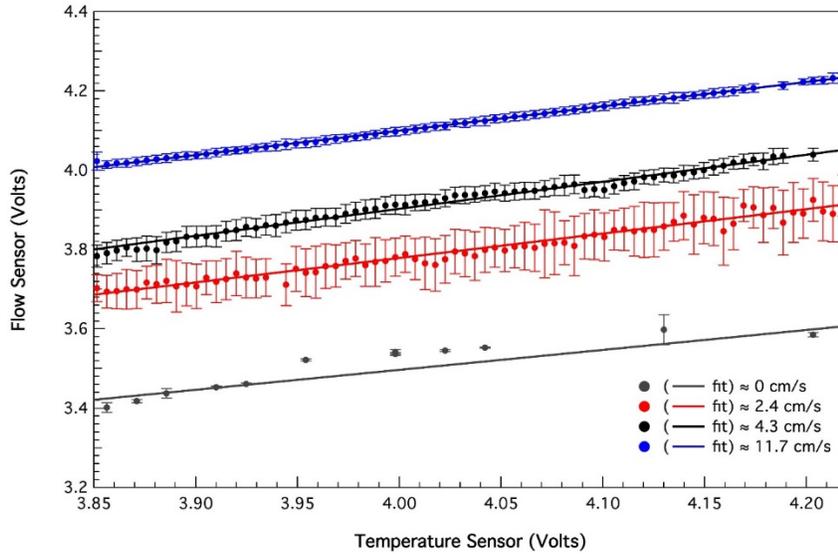


Figure 10. Temperature dependence of flow sensor at different flow velocities. The data for each flow velocity were fit to a linear function. Error bars represent standard deviation.

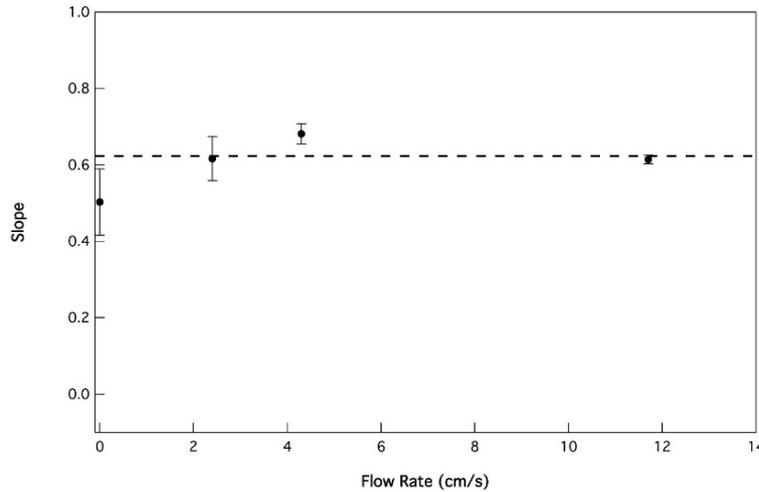


Figure 11. Slope of fitted lines from Figure 10 versus calculated flow velocity. The dashed line (-----) represents the average of the observed slopes. Error bars represent standard deviation.

The internal flow as measured by the sensor using the calibrations shown in Figure 9 compared to external flow velocity as measured by the ADV is shown in Figure 12. These measurements establish that the sensors, due to their small form factor, can be interfaced inside of a POCIS canister to monitor the local flow velocities in the vicinity of the POCIS. The data for each set of sensor measurements were independently fit to $f(x) = ax$, since at the static flow condition the internal and external flow rates will be 0 cm/s. For both sets of sensor measurements, the slopes were statistically equivalent, thus the data sets were combined to yield the fit shown in Figure 12 with a slope of 0.40 ± 0.02 . At the measured location within the POCIS canister, the internal flow velocity is reduced by a factor of 2.5 with respect to the external flow velocity. This flow velocity reduction demonstrates that measurements of the external flow velocity are inadequate at capturing the hydrodynamics within a POCIS canister. Thus, to properly quantify and account for the flow effects on POCIS during deployment,

measurements of the flow within the canister should ideally be collected concurrently during sampling.

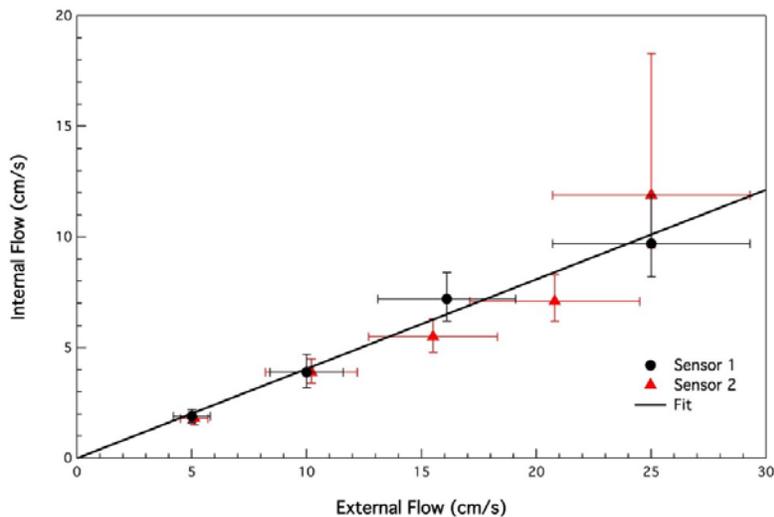


Figure 12. Comparison of flow velocities internal and external to POCIS canister for two independent measurements using *Sensor 1* and *Sensor 2*. The data are fit to $f(x) = ax$ with $a = 0.40 \pm 0.02$. Error bars represent standard deviation.

Conclusions and Implications for Future Research

Four approaches for reducing the impact of variable flow rate on sampling rate were tested as summarized in Table 3. As noted in the results, three approaches were promising and proof of concept was obtained. Including flow reducing screens, PRC, and flow sensors. PRCs require a significant amount of analytical chemistry to be performed during manufacture and the ability of laboratories to analyze compounds outside of their standard analyses. Both flow reducing screens and flow sensors are expected to be robust options that can be readily developed and have very good likelihood of successful technology transfer because they could be brought to full prototype with a minimal, but realistic level of funding. A negative aspect of flow reducing screens is that additional testing related to fouling and calibration will be necessary. Acceptance would likely depend on the result of these studies. If new sampling rate studies are required, then users may prefer the traditional POCIS where rates are already available for many analytes including MCs.

Table 2. Proof of concept success and potential for further development of the approaches tested.

Approach	Proof of Concept Success	Remaining Effort Required to Have Final Prototype	Technology Transfer Potential
Double membrane	No - Unlikely that thickening the membrane will be effective without major reduction of sampling rate.	No effort suggested	No transfer suggested
Flow reducing screen	Yes – Resulting sampling rates were very similar with the screen in place.	Optimization of pore size and testing for other screen materials such as stainless steel. New calibrations will be required for all analytes of interest. Test for fouling and performance in the environment required.	Despite decreased effort to determine accurate sampling rates, acceptance at the commercial level is unknown depending on the need for new sampling rates to be determined.
Performance Reference Compound	Yes – For most analytes PRCs resulted in improved calibration across flows; however, a few important analytes such as RDX were not improved.	Stability testing to determine if PRCs are stable during shipping and storing. Consider more potential PRCs to compensate for RDX. Further calibration under different environmental conditions.	Could be difficult. Commercial providers appear to be reluctant as there is not a consensus choice of PRC. Addition of compounds to the sampler would likely be a custom process. Moreover, the PRC will require additional analyses cost at the analytical labs as they will not be on current analytical lists.
Flow Sensor	Yes – A promising sensor design was found and tested	Further development of electronics and water proofing. Testing under angular flow.	The device could be broadly applicable to numerous aquatic studies even beyond passive sampling. Thus, we expect interest in commercial transfer.

Our positive results to date indicate that we are close to enabling a robust, modified POCIS for service in even challenging environments. To fulfill our overall objective of developing a sampler for use in the epibenthic environment, we also need to evaluate modified POCIS approach in this environment. Partitioning to the water will be a driving factor for MC toxicity and transport. Comparison of epibenthic POCIS measurements to sediment and pore water concentrations in controlled exposure scenarios will provide a great deal of information on how to optimize POCIS for future field monitoring. If detection of sediment contamination is possible through epibenthic measurements with POCIS, sampling and analysis of sediment with unknown UXO sources can be minimized.

Proposed Future Research Efforts

Our future efforts will be primarily targeted at further development of the flow sensor, calibration of the flow sensor, comparison of flow sensor readings to simultaneously measured POCIS sampling rates, and incorporating flow sensors into deployment cages. Development of the primary flow sensor system will likely require a little over a year. Calibration, testing, and demonstration of the system will take another year. Flow sensors need to have several components developed and integrated to form a fully functioning prototype including supporting electronic subsystems to provide power and data acquisition capabilities for portable, unattended

deployments; combined water proofing of sensor, supporting electronic subsystems, and system interfaces; angular flow dependence; and deployment hardware. Most of this work will be laboratory based followed by a few larger flume experiments to test the completed system under varying flow conditions.

An additional step in the development of the approach is to evaluate how POCIS can best be utilized when MC sediment contamination is present. A modified deployment cage may be necessary to better allow contamination measurement from sediment associated MC. Comparison of sediment concentration, pore-water concentration, and POCIS measurement will allow a better understanding of the role POCIS can play at contaminated sites and what other measurements would be needed. To allow these comparisons, large scale spiked sediment studies using large tanks with high water turnover will be used.

Literature Cited

- Belden JB, Lotufo GR, Biedenbach JM, Sieve KK, Rosen G. 2015. Application of POCIS for exposure assessment of munitions constituents during constant and fluctuating exposure. *Environmental Toxicology Chemistry* 34:959-967.
- Chappell, M.A., Price, C.L., George, R.D. 2011. (Editors) *Environmental Chemistry of Explosives and Propellant Compounds in Soils and Marine Systems: Distributed Source Characterization and Remedial Technologies*. ACS Symposium SERIES 1069, American Chemical Society.
- Chen, CE, Zhang H, Ying GG, Jones KC, 2013. Evidence and recommendations to support the use of passive water sampler to quantify antibiotics in wastewaters. *Environ. Sci. Technol.* 47:13587-13593.
- Bopp S, Weib H, Schirmer K. 2005. Time-integrated monitoring of polycyclic aromatic hydrocarbons (PAHs) in groundwater using the Ceramic Dosimeter passive sampling device. *Journal of Chromatography A* 1072: 137-147.
- Cristale J, Katsoyiannis A, Chen C, Jones K, Lacorte S. 2013. Assessment of flame retardants in river water using a ceramic dosimeter passive sampler. *Environmental Pollution* 172:163-169.
- Conder, J. M., La Point, T. W., Lotufo, G. R., and Steevens, J. A. (2003) Nondestructive, minimal-disturbance, direct-burial solid-phase microextraction fiber technique for measuring TNT in sediment. *Environmental Science and Technology* 37: 1625-1632.
- Harman C., Allan, I.J., Bauerlein P.S. 2011. The challenge of exposure correction for Polar Passive Samplers – The PRC and the POCIS. *Environmental Science and Technology*. 45:9120-9121.
- Harman, C.; Allan, I. J.; Vermeirssen, E. L. M. (2012). Calibration and use of the polar organic chemical integrative sampler-A critical review *Environ. Toxicol. Chem.* 2012, 31, 2724–2738.
- Lewis, J., R. Martel, L. Trepanier, G. Ampleman, S. Thiboutot. 2009. Quantifying the transport of energetic materials in unsaturated sediments from cracked unexploded ordnance. *J Environ Qual* 8:2229-2236.

- Li, H., Vermeirssen L.M., Helms, P.A., Metcalfe C.D. 2010. Controlled field evaluation of water flow rate effects on sampling polar organic compounds using Polar Organic Chemical Integrative Samplers. *Environmental Toxicology and Chemistry*. 29:2461-2469.
- Li, S., George, R.D., Hihara, L.H. 2016. Corrosion analysis and characteristics of discarded military munitions in ocean waters. *Corrosion Science* 102:36-43.
- Liu, H., Wong, C.S., Zeng, E.Y. 2013. Recognizing the limitations of performance reference compound (PRC)-calibration techniques in passive water sampling. *Environmental Science and Technology* 47:10104-10105.
- Lotufo G.R., Lydy M.J., Rorrer G.L., Cruz-Uribe O., Cheney D.P. (2009). Bioconcentration, bioaccumulation and biotransformation of explosives and related compounds in aquatic organisms. In
- Lotufo G.R., Rosen G., Wild W. 2013. Summary Review of the Aquatic Toxicology of Munitions Constituents. ERDC Technical Report. ERDC/EL TN-13-8. US Army Engineer Research and Development Center, Vicksburg, MS.
- Lynch, JC, Brannon, JM, Delfino, JJ. 2002. Effects of component interactions on the aqueous solubilities and dissolution rates of the explosive formulations Octol, Composition B, and LX-14. *J Chem Eng Data*. 47:542-549.
- Mazzella, N., Debenest, T., and Delmas, F. (2008) Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment. *Chemosphere* 73: 545-550.
- Morin, N., Mie`ge, C., Random, J., Coquery, M., 2012. Chemical calibration, performance, validation and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments. *TrAC Trends in Analytical Chemistry* 36:144-175.
- NAVFAC (2009). Ecological Risk Assessment. Tier 2 Steps 3B&4: Problem formulation, study design (DQOs), and work plan. Supplemental Remedial Investigation at Operable Unit 2. Jackson Park Housing Complex/Naval Hospital Bremerton. Prepared by Tetra Tech EC, Inc., Contract N44255-01-D-2000. September 1, 2009.
- O'Brian, D.S., Booij, K., Hawker, D.W., Mueller, J.F. 2011. Method for the in-situ calibration of a passive phosphate sampler in estuarine and marine waters. *Environmental Science and Technology* 45:2871-2877.
- Pascoe G.A., K. Kroeger, L. Leisle, and R.J. Feldpausch 2010. Munition Constituents: Preliminary Sediment Screening Criteria for the Protection of Marine Benthic Invertebrates”, *Chemosphere* 81, 807-816.
- Rosen G, Belden J, Lotufo GR, Wild W. 2012. Application of Passive Sampling Devices for Underwater Unexploded Ordnance Exposure Assessment. Presentation at the 33rd Annual SETAC Meeting, Nov 11-15, 2012. Long Beach, CA.
- Rosen G., Lotufo G.R. 2010. Fate and effects of TNT and RDX released from Composition B in multi-species marine exposures. *Environmental Toxicology and Chemistry*, 29 (6): 1330-1337.
- Seethpathy S, Gorecki T, Li X. 2007. Passive sampling in environmental analysis. *Journal of Chromatography A*. 1184:234-253.
- Sunahara G.I., Lotufo G.R., Kuperman R.G., Hawari J., editors. 2009. *Ecotoxicology of Explosives*. CRC Press. Boca Raton, FL, p. 135-156.

- USACE 2012. Draft Report: Ecological Risk Assessment: Ordnance Reef (HI-06) Wai‘anae, O‘ahu, Hawai‘i. U.S. Army Corps of Engineers. Contract No.: N00024-08-D-6323. November 2012.
- USEPA. 2007. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846
- Wang, P.F.; Liao, Q.; George, R.; and Wild, W. “Defining Munition Constituent (MC) Source Terms in Aquatic Environments on DoD Ranges (ER-1453)”, SSC Pac TR# 1999, January 2013, 130 pp.
- Zhang, B., X. Pan, J. N. Smith, T. A. Anderson, and G. P. Cobb. 2007. Extraction and determination of trace amounts of energetic compounds in blood by gas chromatography with electron capture detection (GC/ECD). *Talanta* 72:612-619.