Monitoring Munitions Constituents in Underwater Environments Using Passive Sampling Devices

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Background/Objectives. As a result of military activities, underwater military munitions (UWMM), as unexploded ordnance (UXO) or discarded military munitions (DMM), are present in underwater environments. UWMM may contain munitions constituents (MC) such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), which are among the most widely used high explosives. If UWMM becomes corroded or breaches, the fill material may leak or dissolve into the surrounding environment, potentially adversely affecting the exposed biota. In large part because of the high cost and complexity associated with sampling MC at UWMM sites, detailed and reliable information about MC in water is available for only few sites and temporal and spatial uncertainties persist.

Approach/Activities. This research focused on the optimization and field validation of a commercially available in situ passive sampling device, the Polar Organic Chemical Integrative Sampler (POCIS), for detection and quantification of MC in underwater environments. POCIS provides integrative, continuous sampling in situ, and ultra-low detection limits and potentially more meaningful time-weighted averaged (TWA) water concentrations, compared with more traditional sampling (e.g. grab) methods. Laboratory studies determined sampling rates ($R_s$) for multiple MC under different flow velocities and biofouling conditions. Laboratory studies were followed by two unique field demonstration efforts. The first involved the point source placement of a known quantity of the explosive fill material Composition B (39.5% TNT, 49.5% RDX, 1% wax) at an uncontaminated estuarine site. The controlled study was followed by placement of POCIS within the Live Impact Area at the former Vieques Naval Training Range at Bahia Salina del Sur (Vieques, Puerto Rico), a bay with documented high incidence of munitions items including UXO. The Vieques study design involved POCIS placement within approximately 15 cm of 15 potentially leaking UXO, and an unbiased (i.e., a grid design over a ~200 acre area) placement, also 15 locations, in the bay.

Results/Lessons Learned. Sampling rate increased with flow rate for all MC investigated, but flow velocity had the strongest impact on TNT ($R_s$ for 30 cm/s was significantly higher than that for 7 cm by a factor or 2.7) and the weakest impact on RDX. No significant differences in uptake of TNT (or RDX were observed across a gradient of biofouling presence. For the controlled study, TWA concentrations for TNT and RDX determined using POCIS ranged from 9 to 103 ng/L, with the highest concentrations nearest the Composition B source, but all samplers positioned greater than 2 m from the source resulted in non-detects. For the demonstration study in Vieques, TWA concentrations for TNT and RDX were observed at ultra-trace concentrations ranging from 0.004 to 0.013 µg/L, except adjacent to an apparent leaking UXO where the TNT TWA concentration was 5.3 µg/L. Measured concentrations were substantially lower than ecological risk thresholds derived from recently updated species sensitivity distributions for these constituents.