Evaluation of Equilibrium Passive Sampling Polymers for Monitoring Munition Constituents in Aquatic Systems

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Background/Objectives. A wide array of military munition constituents are present in water bodies surrounding historically deposited unexploded ordnance. A common approach for monitoring explosive constituents involves the collection of large quantities of discrete water samples combined with solid phase extraction to ensure sufficient sensitivity and detection. More recently, polar organic chemical integrative samplers (POCIS) have been tested for in situ assessments of munition constituents at underwater sites. However, POCIS requires extensive calibration prior to exposure in the field (i.e., determination of sampling rates). Simple and sensitive monitoring efforts are therefore necessary to better understand the bioavailability and potential long-term bioaccumulation and toxicity of military munition constituents in different aquatic environments. The objectives of this study were (1) to test the nonpolar polymers polydimethylsiloxane (PDMS), low density polyethylene (LDPE), and polyoxymethylene (POM), and a relatively polar ethylene vinyl acetate (EVA) as equilibrium passive samplers for measuring the C\text{free} of munition constituents, and (2) to investigate and compare the use of POCIS sorbents including Oasis HLB, Ambersorb and Isolute Env+ in an equilibrium sampling approach.

Approach/Activities. All polymer materials were successfully loaded in methanol followed by solvent evaporation with the munition constituents 1-nitroguanidine, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2-amino-4,6-dinitrotoluene and tetryl serving as performance reference compounds (PRCs). Loaded polymers were exposed in batch water systems spiked with the munition constituents 4-amino-2,6-dinitrotoluene, pentaerythritol tetranitrate (PETN) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). The release and uptake of explosive compounds was monitored in polymer and water phases over time using HPLC-MS.

Results/Lessons Learned. Preliminary results suggest that the stronger affinity of PETN to PDMS may be explained by its higher octanol-water partition coefficient (log K\text{OW} = 3.7) as compared to other munition constituents in the water phase, and thus favored hydrophobic interactions with the polymer. On the contrary, dissipation of preloaded RDX (log K\text{OW} = 0.9) was much faster compared to 1-nitroguanidine (log K\text{OW} = -0.89), and likely not governed by compound hydrophobicity. The presentation provides information both on the uptake and release of explosive compounds to a variety of polymeric materials and discusses their potential for application in equilibrium passive sampling.