

Background/Approach: In recent years, we have been evaluating the historic use of polycyclic aromatic hydrocarbon (PAH) containing clay targets at Navy/Marine skeet ranges for purposes of exposure characterization and risk assessment, with a Example clay target (a), fragmented clay target (b), focus on PAH composition, soil-skeet partitioning, and bioavailability associated with incidental digestion of such soils. Relative and soil containing clay target fragments (c). bioavailability (RBA) is a frequently used risk characterization approach that is indicative of the amount of PAH available to an (a) organism divided by the amount of PAH extracted using organic solvent(s). In the absence of digestive bioavailability or uptake information, the RBA value is typically assigned a value of 1, which can be overly conservative by up to an order of magnitude in many cases. The conventional approach consists of feeding trials using site-specific PAH-contaminated soils to ascertain the uptake of PAHs by the organism itself. However, such an approach is cost and time-prohibitive, resulting in a need for development of better tools and methodologies that provide a faster and cheaper means to characterize the biological uptake Skeet Range of PAHs from soils. A central goal of our efforts is to explore strategies to more efficiently determine an accurate RBA value for skeet and PAH-associated soils at these ranges. Our efforts have been focused on evaluating two approaches that can be used to characterize the PAH bioavailability, a acres/ site. Physiologically Based Extraction Test (PBET) that extract PAHs from soil using a simulated digestive matrix, and a commercially-available polyethylene passive sampling device (PSD) that determines freely-dissolved PAHs in soil. **Technical Objectives:** Determine the polycyclic aromatic hydrocarbon (PAH) **Relative Bioavailability** composition of clay targets and the relative bioavailability in soil using: For a given environmental exposure: • PBET RBA **RBA** = PAHs absorbed by humans /PAHs by Passive sampler equivalent RBA EPA standard extraction Standard Extraction – EPA 3541 or 3545 **Benefits:** Will provide sites with an improved ability to discern clay target particles extraction with a 8270C GCMS; Extraction from soil, and fate and transport of PAHs. Chemicals – *acetone & n-hexane* • Provide more realistic/site specific RBAs for PAHs and not default RBAs Current assumed RBA = 1; Studies suggest actual RBA ~0.1 to 0.76 • Provide technical information that RPMs can use to negotiate lower risk based clean-up levels. Cost savings for the Navy could be significant as there are multiple sites requiring potential clean up. At a rate of approximately \$200-300/CYD, this **Primary factors impacting RBA:** would cost over \$1-1.5M per site. Bioavailability of PAHs bound to skeet fragment Reduced site clean-up could result in saving of \$400K-\$1.2M per site. Differentiation of skeet & soil particles Skeet and soil particle size analysis PBET (a) and passive sampling (b) approaches to Variety of extraction methods/chemicals concentration of freely-dissolved (Cfree) B(a)P in soil (b). evaluate chemical availability of B(a)P in soil. **(a)** Bioavailability of PAHs bound to soil **(**a) Skeet fragment weathering **—** Release of PAHs **Basic scheme of Physiologically Based Extraction Test (PBET)** -0.5 Skeet Fragment -1.0 1 g soil spiked with PA Soil Particle 3(a)P Excr r = 0.86 x - 2.389 ml saliva PAHs $R^2 = 0.94$ PAH/Soil binding *P* = 0.005 pH 3.0 14 ml gastric juice -2.5 Log₁₀ Urina **Physiologically Based Extraction Test (PBET)** 27 ml duodenum juice + 7 ml bile pH 7.0 + 7 ml bile Digestion 1 g, dw soil extracted via (Stomach) **Passive Sampling** simulated digestion and 2.0 1.0 Centrifuge excretion process Log₁₀ [PBET B(a)P] Theory versus total Analysis of B(a)P in resulting Further Digestion/ Supernatant extract Excretion Cfree has been shown to be a good predictor of dermal uptake of PAHs Average Relative Bioavailability (RBA), based on urinary excretion rate (above), 100.0 PAH in soil (mg/kg) regardless of PAH source 80.0 versus the concentration of B(a)P in PBET extract (a), the concentration of freely-(e.g., solvent, fuel oil skeet, soot) dissolved (Cfree) B(a)P in soil (b), and the soil-Cfree partition coefficient (Kd), as **Dermal PAH** oioavailabilit Cfree should also versus Cfree determined with Cfree and the concentration of B(a)P in soil (c). correlate with digestive (direct correlatio availability (a) (b) 70% -70% (b) 60% 60% -Figure 5. PHE and B(a)P flux through pig skin as a function of 60% ation in soil (A) and equilibrium aqueous concentration (B). $R^2 = 0.81$ Xia et al. 2016, Environ. Sci. Technol. 50:3444-3452 y = -0.12x + 0.3850% 50% 50% *P* = 0.04 y = -0.19x + 0.33Fixed calibration issue $R^2 = 0.54$ R² = 0.64 P > 0.05 **Vag** (%) 40% **40%** (%) Getting ~80% recovery **Yay** (%) 40% *P* > 0.05 on BaP and other 30% 30% 30% PAHs 20% 20% 20% 10% 10% 10% 0% 2.0 0.0 3.0 1.0 6.0 6.5 -1.0 -1.0 00 2.0 5.0 Freely-dissolved (Cfree) Log₁₀ [PBET B(a)P] Log₁₀ [Cfree B(a)P] Log₁₀ Kd **Acknowledgements** Passive Sampling (L/kq) **NAVFAC:** John Schoolfield. PE • 80 g, dw soil exposed to polyethylene passive William Major – PI (Retired) sampler (SP3[™], www.siremlab.com), 14 U.S. Army Corps of davs **Engineers:** Anita Meyer, PhD associated PAHs are much less available than soils spiked with petroleum- and solvent-borne PAHs, respectively. The PBET and PSD results from skeet-PAH soils have also been • Analysis of B(a)P in (leveraged partner) Directorate of sampler and conversion to compared on the basis of benzo(a)pyrene with results of dose-response and RBA estimates from feeding trials using those same soils. The use of these tools appears to be a valuable **Environmental and Munitions Center** Cfree approach for purposes of determining bioavailability of PAHs in soils for accurate RBA estimation and risk characterization. We are currently evaluating a broader suite of PAHof Expertise Arcadis – Glenn C. Hoeger impacted soils to assist in the development of a robust empirical model for correlating RBA estimates from PBET and PSDs with RBA estimates from feeding trials.



PAH Bioavailability Studies of Skeet-impacted Soils

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