PRACTICAL RESEARCH DESIGN FOR SITE-SPECIFIC BIOTA-SEDIMENT ACCUMULATION FACTORS

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Introduction:
Working cooperatively with the US EPA, remediation has been performed at a National Priorities List site on the eastern coast of the USA. The site was impacted by polychlorinated biphenyls (PCBs) and other contaminants of concern. The remediation of this tidal estuarine site included excavation of contaminated soil and sediment and construction of a containment wall. The sediment at the site contains PCBs and other chemical contamination that potentially could be accumulated in the tissues of benthic invertebrates.

As part of the long-term monitoring to determine the effectiveness of the remedy, data were gathered on tissue and sediment contaminant concentrations. These studies are designed to support the determination of site-specific biota-sediment accumulation factors (BSAFs). The objective of the current and future studies is to collect, in a practical manner, sufficient data to determine location-specific BSAFs for a systematically selected set of PCB congeners, to ensure that they are sufficiently low and not increasing over time.

The measured values are being obtained via *in-situ* bioaccumulation studies in which caged *Lumbriculus variegates* are exposed to sediments in tidal mud-flats for 28 days at four test sites and two reference sites. The proper construction, deployment, and care of the *in-situ* caged invertebrate exposures require frequent site visits, significant labor, and cost. Finally, weather events and vandalism cannot be absolutely prevented, and therefore, an alternative approach is being evaluated.

Published literature has reported a relationship between near-equilibrium partitioning to polyethylene (PE) and polyoxymethylene (POM) sheet samplers and partitioning to benthic invertebrates. Jonker, *et al*., reported a direct relationship between log KPOM and log KOW.[1] Vinturella, *et al*., reported the use of PE for PAHs in polychaetes and observed promising correlations with biouptake and cited practical advantages over semi-permeable membrane devices (SPMDs).[2] Burgess, *et al*., compared PCB concentrations in several polymer sheet configurations to caged blue mussel concentrations in New Bedford Harbor, including PE, polydimethyl siloxane (PDMS) sheets and SPMDs,[3] and notable correlations, especially with PE and PDMS. Fagervold, and Ghosh, *et al*., found compelling correlations between POM samplers and earthworm concentrations.[4] Heijden and Jonker 2009, compared a variety of samplers for relationships with uptake in *Lumbriculus variegates* and found *in-situ* PDMS solid phase microextraction fibers (SPME) and *in vitro* POM sheet samplers to be the best predictors.[5]

The parallel use of *in-vitro* passive sampler is proposed to determine whether this technique may be used as a more secure, less expensive, yet valid alternative to the caged worm studies. The research design and quality assurance/quality control approaches developed to determine usability of the data are presented herein.

Materials and Methods:
The test chambers were constructed of 10-cm cellulose acetate butyrate tubing cut to 30-cm length; 30 to 40 holes were drilled through the wall of each tube. A covering of 80-µm polypropylene mesh was wrapped around the chamber and secured with silicone caulk. Polyethylene end caps with inlet, outlet ports were placed on the ends of the tubes. The cells were soaked in deionized water for at least 24 hours immediately before site installation. Sediment was collected at each of the four study sites and the two reference locations. Each field site (test and control) consists of an identical number of replicate *in-situ* test chambers (six replicates). Approximately 1 gallon of surficial sediment collected from each location was placed inside each test chamber. On the next round of exposures, an aliquot of each sediment sample also will also be set aside for the passive sampler experiment.

As part of the installation of the sediments in the test chambers, obvious indigenous organisms were removed. Once filled with sediment, each test chamber was filled with site water, capped, and secured into position by elastic bands within a wire basket. A 1.2-m length of rebar was driven into the mudflat at each testing location until only 30-cm remained. This provided a uniform method to locate the test chambers if they were to become buried.

After a 3-day period to allow equilibration of water and sediment, a small amount of water was siphoned through the mesh screen from each test chamber and tested *in-situ* for dissolved oxygen (DO) concentrations. At the completion of the DO measurements, approximately 20 g of *L. variegatus* was added to each chamber via the port and the test chambers were returned to their positions. Test chambers were checked several times per week to verify that the correct test chamber positioning was being maintained. Each test chamber was checked for damage (*e.g.*, holes in the window mesh that would allow escape by test organisms or entry by indigenous organisms). After 28 days of deployment, the worms and sediment were removed and gently rinsed with cool water to facilitate collection of live specimens, which were then depurated and transferred to the analytical laboratory.

The live worm samples were sacrificed, homogenized , spiked with 13C-labeled PCB congeners, and extracted in accordance with US EPA Method 1668A. The extract was split for gravimetric lipids determination. The remaining extract was subjected to gel permeation chromatography (GPC), silica gel and Florisil™ cleanups, to be analyzed by high resolution mass spectrometry (HRGC/HRMS).

The sediment samples to be collected at the beginning of the next deployment will be extracted and analyzed for PCBs and total organic carbon. Another aliquot of the sediment (100 g dry weight) will be placed in a 1-L amber glass passive sampler cell with a hexane pre-extracted strip of 53 µm polyoxymethylene (POM) of a determined mass targeted at 0.20 g. This sampler will be placed in the cell, along with 900 mL of site water and 1 g of sodium azide. The cell will be sealed with a PTFE-lined lid and placed on a cell roller. The cell roller is rotated at 3 rpm for 28 days. The POM will then be retrieved, and the surface will be wiped clean of any residue, with a clean, dry tissue. The POM sampler will be extracted and analyzed in the same manner as the sediment and worm tissues - sans GPC because little or no lipids were expected to be present in the extract.

The data provided by the laboratory will be validated by Environmental Standards chemists and then evaluated for usability according to the following criteria:

- If the exposed sample result is less than 10-times the concentration in unexposed samples, the PCB congener is disqualified from BSAF calculations.
- PCB congener results must be resolved chromatographically from other, potentially interfering congeners.
- A validated detection is required for tissue and sediment from the same site.
- These values should be above the practical quantitation limit and (with the exception of sediments and tissues from the two reference locations) should be at least 10-times the levels in the associated blank, equipment blank, and unexposed tissue.

If insufficient data are available under these constraints to calculate at least 10 BSAFs, spanning the predominant levels of chlorination found in the tissues, co-eluting congener sets may be considered as supporting data.

A rigorous QA/QC program was established via a Quality Assurance Project Plan. This provided specific control limits and other performance criteria for method blanks, laboratory control samples, matrix spikes, matrix spike duplicates, initial and continuing calibrations, and independent verification of the calibration standards.

The calculation of BSAFs is described in Burkhard[6], based on Ankley, *et al*.[7] The BSAF is determined by Equation 1, using four measured values:

$$\text{Equation 1: } BSAF = (C_O / f_L) / (C_S / f_{SOC})$$

Where:
C_O is the concentration of the chemical in the organism on a wet weight basis.
f_L is the lipid content of the wet tissue.
C_S is the concentration of the chemical in the sediment on a dry weight basis.
f_{SOC} is the organic carbon content of the dry sediment.

The measured values were obtained via *in-situ* bioaccumulation studies in which caged *Lumbriculus variegates* were exposed to sediments in tidal mud-flats for 28 days. As described above, analytical determination of PCB congener concentrations in the sediment and worms and total organic carbon in the sediment and lipid content in the worms are being collected to establish site-specific biota-sediment accumulation factors for PCB congeners.

Results and Discussion:
For the work described herein, accurate and precise results are expected through a strategic balance between research design and quality program. The rigorous quality program instituted as part of this work consists of a variety of labeled and native PCB congener spikes, replicate samples, and field and laboratory blanks. Inclusion of these QC samples was determined by the authors to be of critical importance in terms of validating and interpreting the analytical data relative to the calculation of BSAFs. Furthermore, the criteria for selection of congeners to be used in the calculations ensures that analytical variability is to be held to a minimum.

The data obtained from these quality control (QC) samples should demonstrate that the study data are a robust high-quality data set. This balance between a rigorous study design and resulting QC sample result should yield study data of known quality at a manageable cost. This balance between the study design and QC regime also allows for a cost-effective opportunity to evaluate the more practical sampling alternative described above.

Acknowledgements:
The authors gratefully acknowledges the contributions of Carlo DiTullio, Steven Langseder, Meredith Langille and Wyn Davies of Arcadis, King of Prussia, PA; and Rich Kling and Robert Blye of Normandeau Associates.

References:
1. Jonker MTO, Koelmans AA. (2001). "Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot." Environ Sci. Technol. 35:3742–3748.
2. Vinturella AE, Burgess RM, Coull BA, Thompson KM, Shine JM. (2004). "Use of Passive Samplers To Mimic Uptake of Polycyclic Aromatic Hydrocarbons by Benthic Polychaetes." Environ. Sci. Technol. 38, 1154-1160.
3. Burgess RM, Zhang Y, McKee MP, Lohmann R, Luey PJ, Friedman CL, Schubauer-Berigan JP, Lefkovitz L. (2008) "Comparison of Passive Sampling Devices for Measuring Dissolved PCBs in the Water Column of a Marine Superfund Site." Proceedings of SETAC North American Meeting.
4. Fagervold SK, Chai Y, Davis J, Wilken M, Cornelissen G, Ghosh U. (2010). "Bioaccumulation of Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans in E. fetida from Floodplain Soils and the Effect of Activated Carbon Amendment." Environ. Sci.Technol. 44, 5546–5552.
5. Van der Heijden SA, Jonker MTO. (2009). "PAH Bioavailability in Field Sediments: Comparing Different Methods for Predicting in Situ Bioaccumulation." Environ. Sci. Technol. 43, 3757–3763.
6. US EPA, Burkhard L. (2009). "Estimation of Biota Sediment Accumulation Factor (BSAF) From Paired Observations Of Chemical Concentrations In Biota And Sediment." EPA/600/R-06/047. ERASC-013F.
7. Ankley GT, Cook PM, Carlson AR, *et al*. (1992). "Bioaccumulation of PCBs from Sediments by Oligochaetes and Fishes: Comparison of Laboratory and Field Studies." Can. J. Fish. Aquat. Sci. 49:2080–2085.