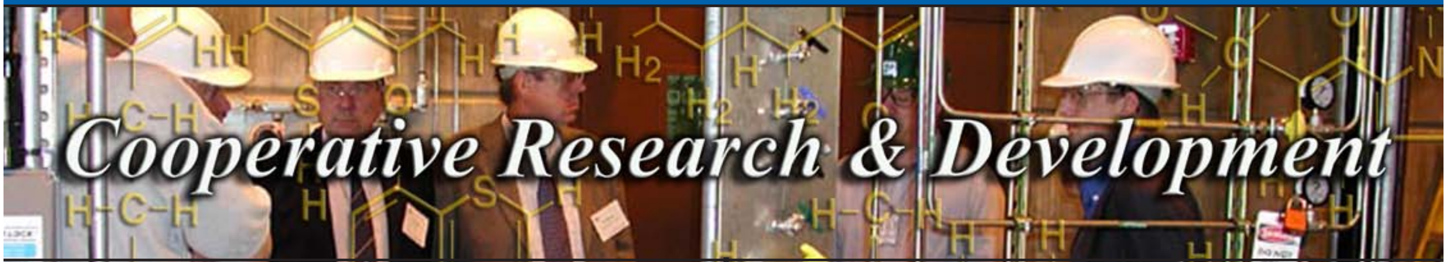

Successes

Better Predictions of PAH Bioavailability in Contaminated Sediments

Advanced Research

To support coal and power systems development, NETL's Advanced Research Program conducts a range of pre-competitive research focused on breakthroughs in materials and processes, coal utilization science, sensors and controls, computational energy science, and bioprocessing—opening new avenues to gains in power plant efficiency, reliability, and environmental quality. NETL also sponsors cooperative educational initiatives in University Coal Research, Historically Black Colleges and Universities, and Other Minority Institutions.

Accomplishments

- ✓ Process innovation
- ✓ Cost reduction
- ✓ Greater efficiency
- ✓ Environmental benefits

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical contaminants from the burning or degrading of coal, gasoline, fuel oil, and such petroleum-based products as asphalt paving. They accumulate in the benthic, or bottom, sediments of watersheds, and can affect bottom-dwelling organisms such as clams and oysters, potentially causing negative health effects in humans and wildlife. Current practices regulating PAHs in sediments are based on total concentrations, rather than the concentrations that are bioavailable. However, recent studies have demonstrated clearly that sediment PAH concentrations cannot be used to predict PAH bioavailability and environmental effects, because of the tight binding of PAHs to contaminated sediments.

In recognition of this problem, the U.S. Environmental Protection Agency (EPA) proposed measuring PAHs in sediment pore water (the water between the sediment particles) as an improved predictor of sediment PAH effects. However, no analytical method existed that could meet the practical requirements of site surveys. In conjunction with an industrial consortium and the U.S. Department of Energy (DOE), the Energy & Environmental Research Center (EERC) has developed the first suitable analytical method to determine pore water PAH concentrations and applied the method to predict PAH bioavailability. The EERC method was compared to toxicity tests on the sensitive benthic organism *Hyalella azteca (H. azteca)* on sediment samples from 14 former manufactured gas plant (MGP) and related industrial sites, and found to greatly improve the prediction of PAH bioavailability compared to existing regulatory practices.

Overview

The Sediment Contaminant Bioavailability Alliance (SCBA) is an industry consortium involving Alcoa, Central Hudson Gas and Electric, Energy East, the EERC, DOE, National Grid, NiSource, the Northeast Gas Association, the U.S. Department of Defense (through the Environmental Securities Technology Certification Program [ESTCP]), and the environmental consulting firm ENSR. This Alliance was established to develop and evaluate the use of chemical measures of contaminant bioavailability for sediment management. The ultimate program goal is to generate a chemical and biological database that can serve as the basis for Federal and state guidance on the use of these chemical measurements for sediment management.

Field data from 14 MGP and aluminum smelter sites show that, even though current regulatory practices rely only on sediment concentrations, toxicity to aquatic organisms is not related to the concentration of total extractable PAHs in sediments using EPA standard methods, as shown in Figure 1.

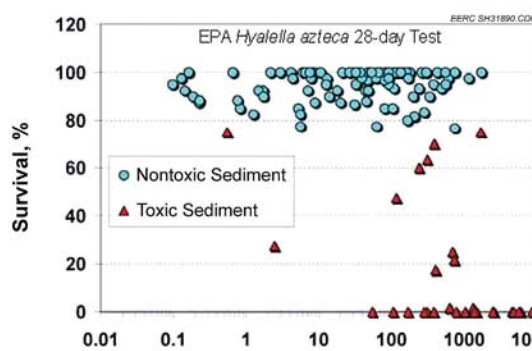

Figure 1 – Bulk sediment total PAH concentration, mg/kg.

Project Duration

Start Date
06/01/05

End Date
12/31/08

Cost

Total Project Value
$1,678,310

DOE/Non-DOE Share
$588,550 / $1,089,760

Industrial Partners

Energy & Environmental Research Center (EERC)
Grand Forks, ND

The RETEC Group, Inc.
Concord, MA

Sediment Contaminant Bioavailability Alliance (SCBA)
http://www.scbaweb.com/

Instead, toxicity is correlated to the concentration of bioavailable PAHs in sediment pore water measured through solid-phase microextraction (SPME) [1], in terms of toxic units (TU), using the method developed by the EERC [2] (see Figure 2). Using this correlation, it is now possible to better predict the exposure and toxicity of PAHs, and perhaps other hydrophobic organics, such as PCBs (polychlorinated biphenyls), in sediments [1]. These concepts are equally applicable for predicting toxicity of organics in soil [3, 4].

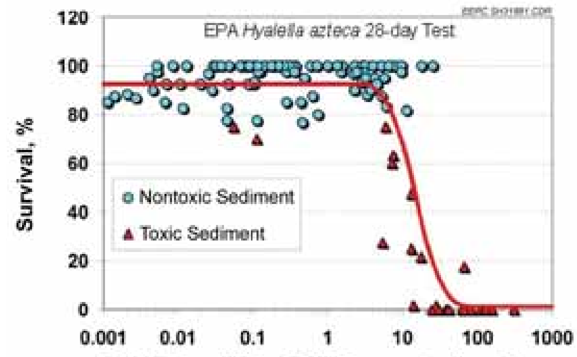

Figure 2 – SPME pore water PAH concentration, TU_{34}.

As demonstrated in the example below, these bioavailability data can be incorporated into predictions of risk and subsequent remedial decisions for sediments, and can ensure that human health and the environment are protected.

Application of EERC/SBCA Methods at Former MGP Site

The bioavailability and toxicity of PAHs in surface sediments were evaluated at National Grid's former MGP site, located on the Hudson River in Hudson, New York. The primary goal of this project was to apply the EERC/SCBA methods to characterize sediments and determine the actual bioavailability and toxicity of PAHs present. Ninety-seven sediment samples were collected and analyzed between 2003 and 2006. The samples were analyzed for total and pore water concentrations of a group of 34 PAHs (called PAH_{34}) identified by the National Oceanic and Atmospheric Administration (NOAA). The PAH_{34} group includes 18 parent PAHs (which include the 16 parent PAHs on the traditional EPA priority pollutant list) and 16 additional groups of alkylated PAHs using EERC methods (2, 5). Total organic carbon (TOC), soot carbon, grain size, pH, and ammonia also were analyzed. The bioavailability and toxicity of PAHs were determined directly by measuring the survival and growth of the aquatic amphipod *H. azteca* following exposure to sediments for 28 days.

The concentration of PAH_{16} compounds was found to range from 3.0 to 8,580 mg/kg. TOC varied from 0.4 percent to 15 percent, and the fraction of TOC composed of heat-stable soot ranged from 10 percent to 84 percent. The data show that PAHs present in surface sediments are not as toxic to benthic organisms as is currently assumed by regulatory sediment screening values of 4.0 (threshold effects concentration [TEC]) and 44.8 mg/kg (probable effects concentration [PEC]). Sediment samples with total PAH_{16} concentrations as high as 750 mg/kg showed no significant reductions in *H. azteca* survival. Clearly, the current EPA screening values for PAHs do not apply to MGP sediments that have a significant percentage of the TOC characterized as heat-stable soot. Application of the equilibrium partitioning (EqP) and hydrocarbon narcosis models (6), adjusted for the bioavailability of PAHs by measuring the pore water PAH concentrations, was effective at predicting toxicity to *H. azteca* using EERC methods (see Figure 3). Reevaluating the sediment data from the Hudson River site in terms of pore water PAH concentrations reduced the area of impact by 85 percent, from approximately 221,000 ft^2 to 31,000 ft^2 (see Figure 4).

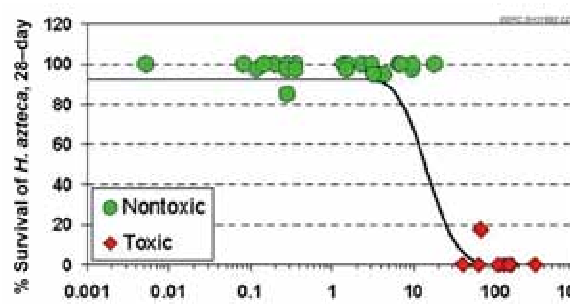

Figure 3 – SPME Pore water PAH concentrations, TU_{34}, predict sediment toxicity to H. azteca at the Hudson, New York, site.

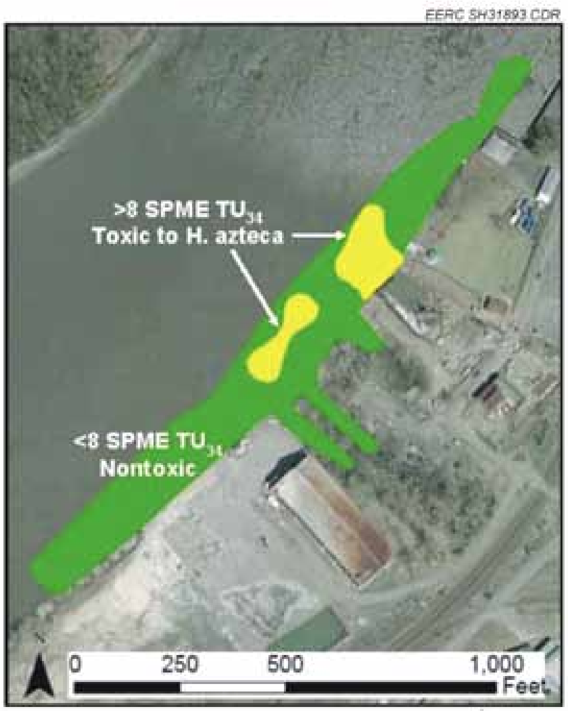

Figure 4 – Using sediment pore water PAH concentrations to delineate impacts focuses remedial design on areas of toxicity.

Project Results and New Initiatives

EERC and SCBA have successfully moved the EERC's SPME pore water analytical technique from R&D status into an active testing protocol, EPA SW-846 (Method 8272); the corresponding American Society for Testing and Materials (ASTM) protocol (D 7363-07) is still provisional, pending a multilab round-robin study. These are the first (and only) agency-approved methods for measuring PAHs in pore water.

The EERC is currently extending its knowledge base toward developing analytical methods for evaluating PCB bioavailability and bioaccumulation by macrobenthic organisms, i.e., those large enough to be seen by the naked eye.

This one-of-a-kind SCBA PAH database continues to add value as a site characterization tool and has direct application in the evaluation of monitored natural recovery as a remedial strategy for sediments. In the sites studied to date, these investigations have demonstrated that remedial actions can be focused on a small fraction of many MGP sites and still be fully protective of human and environmental health.

"This one-of-a-kind SCBA PAH database continues to add value as a site characterization tool and has direct application in the evaluation of monitored natural recovery as a remedial strategy for sediments."

References

1. Hawthorne, S.B.; Azzolina, N.A.; Neuhauser, E.F.; Kreitinger, J.P. "Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to *Hyalella azteca* using Equilibrium Partitioning, Supercritical Fluid Extraction, and Pore Water Concentrations." *Environ. Sci. Technol.* **2007**, *41*, 6297–6304.

2. Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. "Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values." *Environ. Sci. Technol.* **2005**, *39*, 2795–2803.

3. Jonker, M.T.O.; van der Heijden, S.A.; Kreitinger, J.P.; Hawthorne, S.B. "Predicting PAH Bioaccumulation and Toxicity in Earthworms Exposed to Manufactured Gas Plant Soils with Solid-Phase Microextraction." *Environ. Sci. Technol.* **2007**, *41*, 7472–7478.

4. Kreitinger, J.P.; Quiñones-Rivera, A.; Neuhauser, E.F.; Alexander, M.; Hawthorne, S.B. "Supercritical Carbon Dioxide Extraction as a Predictor of Polycyclic Aromatic Hydrocarbon Bioaccumulation and Toxicity by Earthworms in Manufactured-Gas Plant Site Soils." *Environmental Toxicology and Chemistry* **2007**, *26* (9), 1809–1817.

5. Hawthorne, S.B.; Miller, D.J.; Kreitinger, J.P. "Measurement of Total Polycyclic Aromatic Hydrocarbon Concentrations in Sediments and Toxic Units Used for Estimating Risk to Benthic Invertebrates at Manufactured Gas Plant Sites." *Environmental Toxicology and Chemistry* **2006**, *25* (1), 287–296.

6. U.S. EPA. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures*; EPA/600/R-02/013; Office of Research and Development: Washington, DC, 2003.

States and Localities Impacted

Concord, MA

Grand Forks, ND

Hudson, NY

National Energy Technology Laboratory

1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South, Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street, Suite 1400
Tulsa, OK 74103-3519
918-699-2000

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Printed in the United States on recycled paper

June 2008

Contacts

Robert R. Romanosky
Technology Manager,
Advanced Research
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4721
robert.romanosky@netl.doe.gov

Paula B. Flenory
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4781
paula.flenory@netl.doe.gov

Steven B. Hawthorne
Principal Investigator
Energy & Environmental Research Center (EERC)
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018
701-777-5256
shawthorne@undeerc.org