National Association of Remedial Project Managers

Annual Training Program

NARPM

May 24-28, 2010 • Potomac Yard • Arlington, Virginia

20th Anniversary

The Use of SPME in the Lab on Field Collected Sediment to Estimate the Bioavailability of Hydrophobic Organic Sediment Contaminants

Victor S Magar, ENVIRON, vmagar@environcorp.com

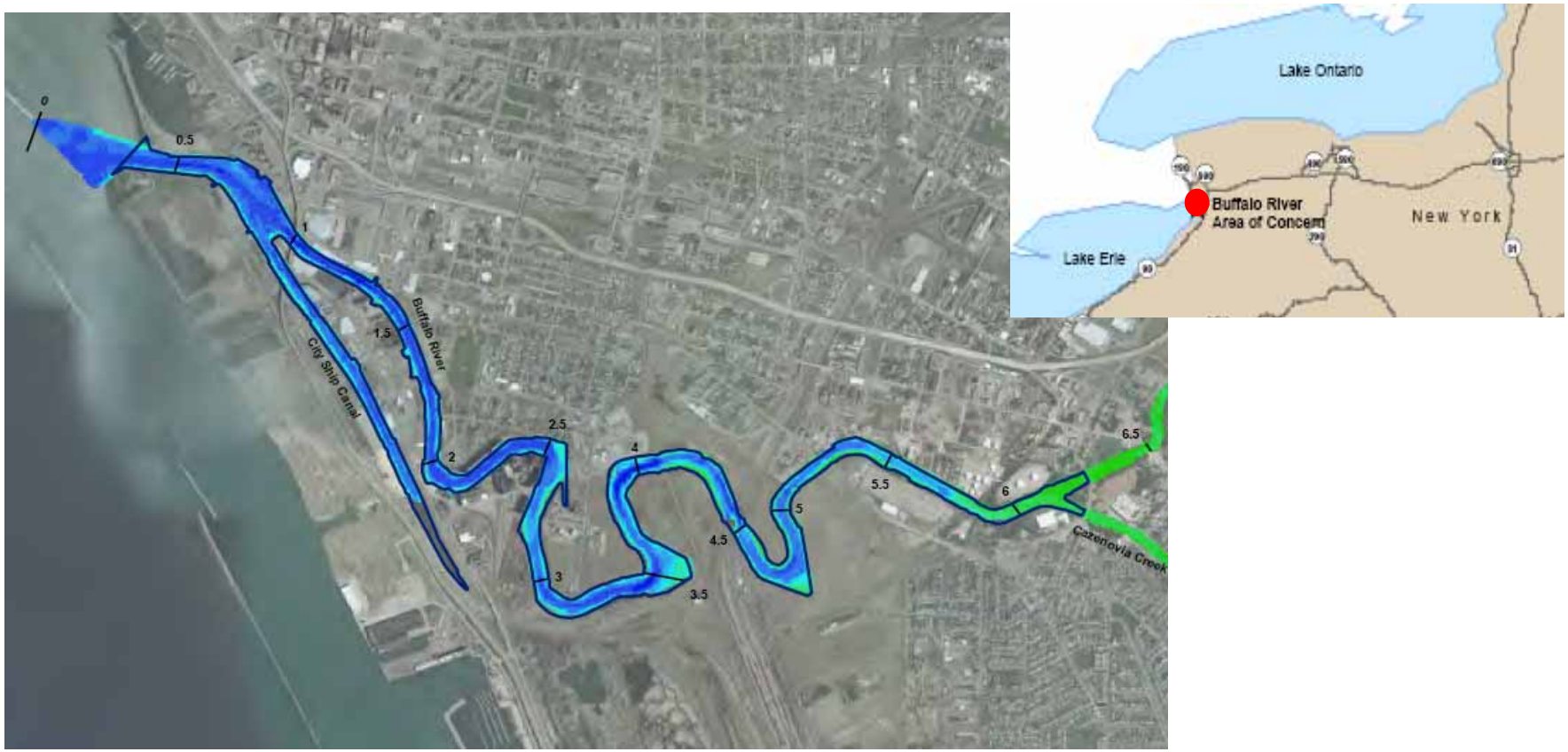
Scott Cieniawski, USEPA, cieniawski.scott@epa.gov

ENVIRON

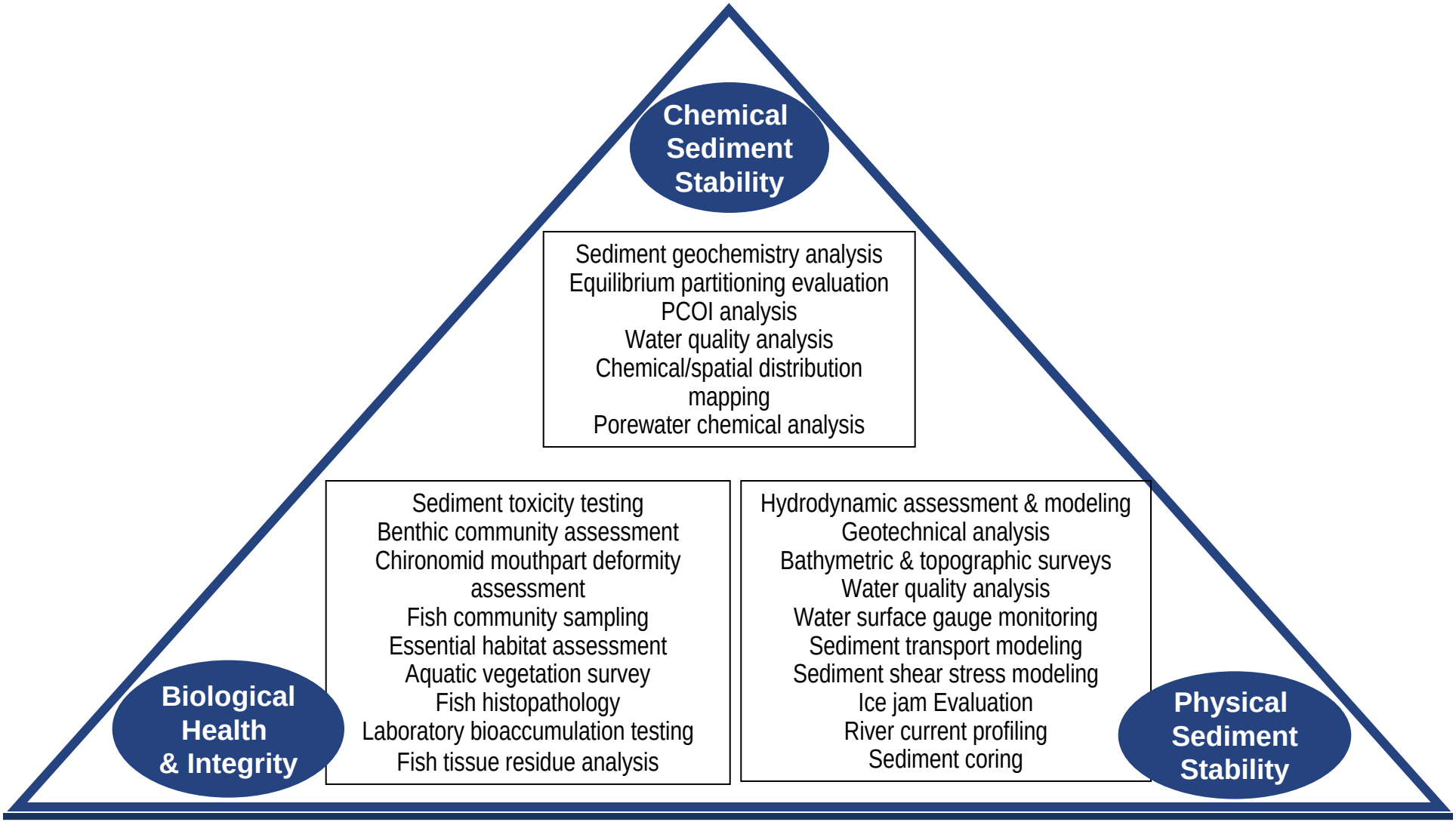
Presentation Outline

- Buffalo River Area of Concern
- Porewater background and scientific principals
- Derivation of PAH Remedial Goals for Buffalo River Sediment
- Other Chemicals Evaluated for Buffalo River Sediment
- Conclusions

Case Study: Buffalo River Area of Concern



Lines of Evidence that Informed Risk Management Decisions for Buffalo River



Buffalo River Chemicals of Concern

- Indicator chemicals of concern (COCs)
  - PAHs
  - PCBs
  - Lead
  - Mercury
- Other COCs
  - PAHs: Benzo(a)anthracene, Benzo(a)pyrene
  - Metals: Arsenic, Chromium, Copper
  - Pesticides: DDT, Gamma-chlordane
- Remedial Goals were developed for the four indicator COCs

Presentation Outline

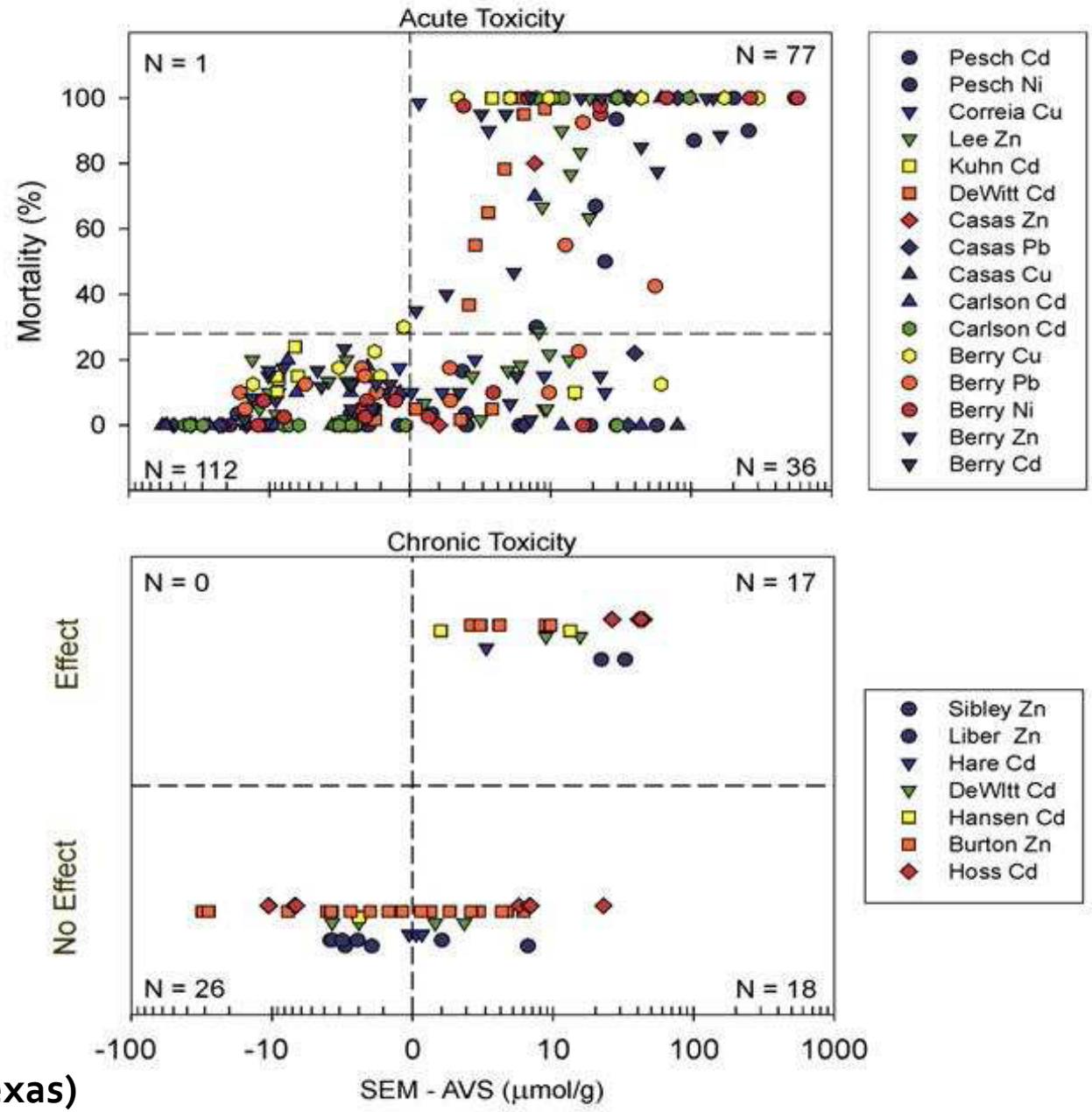
- Buffalo River Area of Concern
- Porewater background and scientific principals
- Derivation of PAH Remedial Goals for Buffalo River Sediment
- Other Chemicals Evaluated for Buffalo River Sediment
- Conclusions

Indicators of Exposure and Risk

- Bulk Sediment Concentration
  - Relatively easy to measure
  - Good indicator of contaminant mass
  - Confusing indicator of risk
  - Largely irrelevant to capping and insitu treatment
- Interstitial Water Concentration
  - Indicator of availability
  - Does not indicate route of exposure

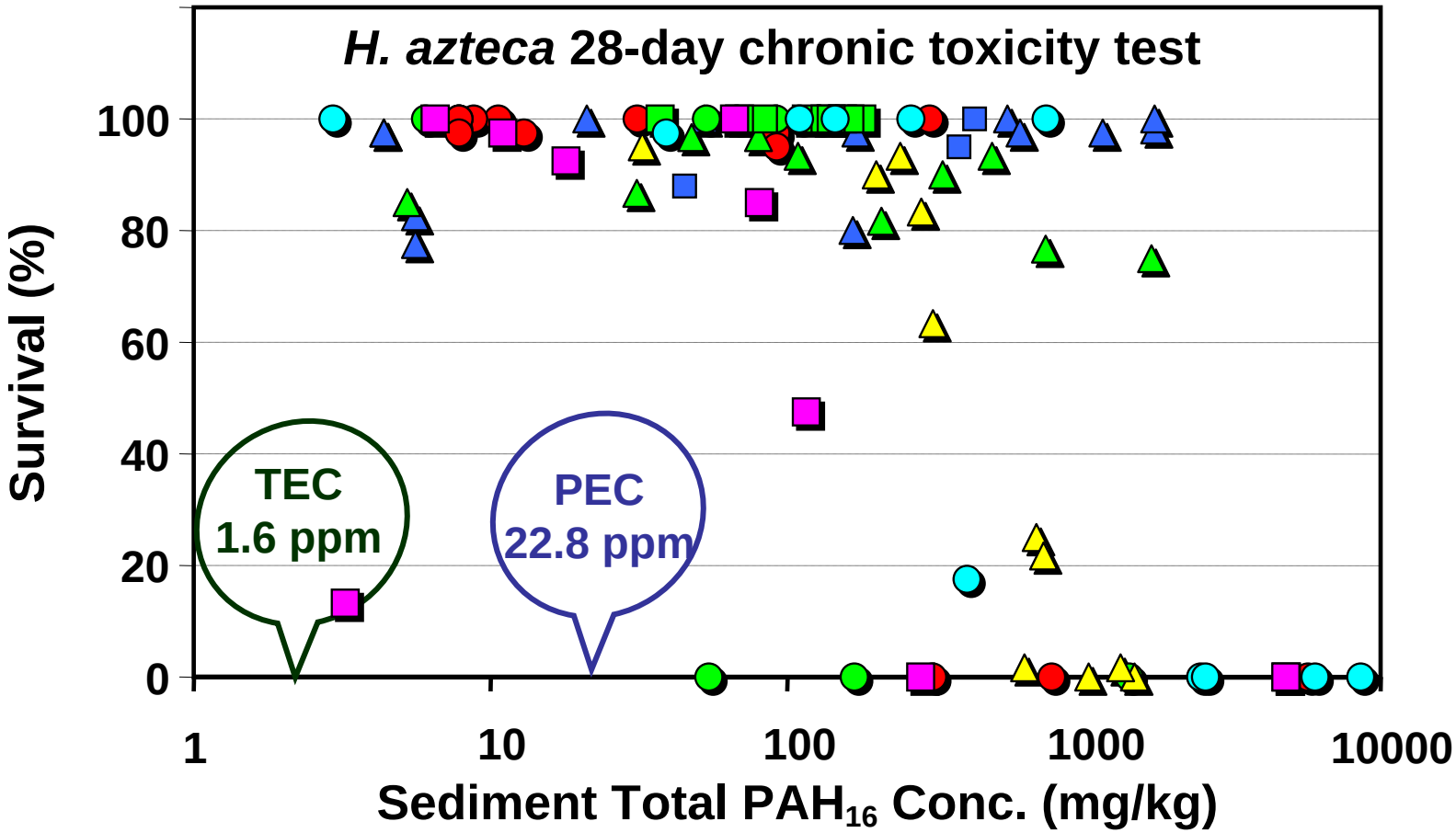
(Courtesy of D Reible, U of Texas)

Metals Toxicity AVS/SEM



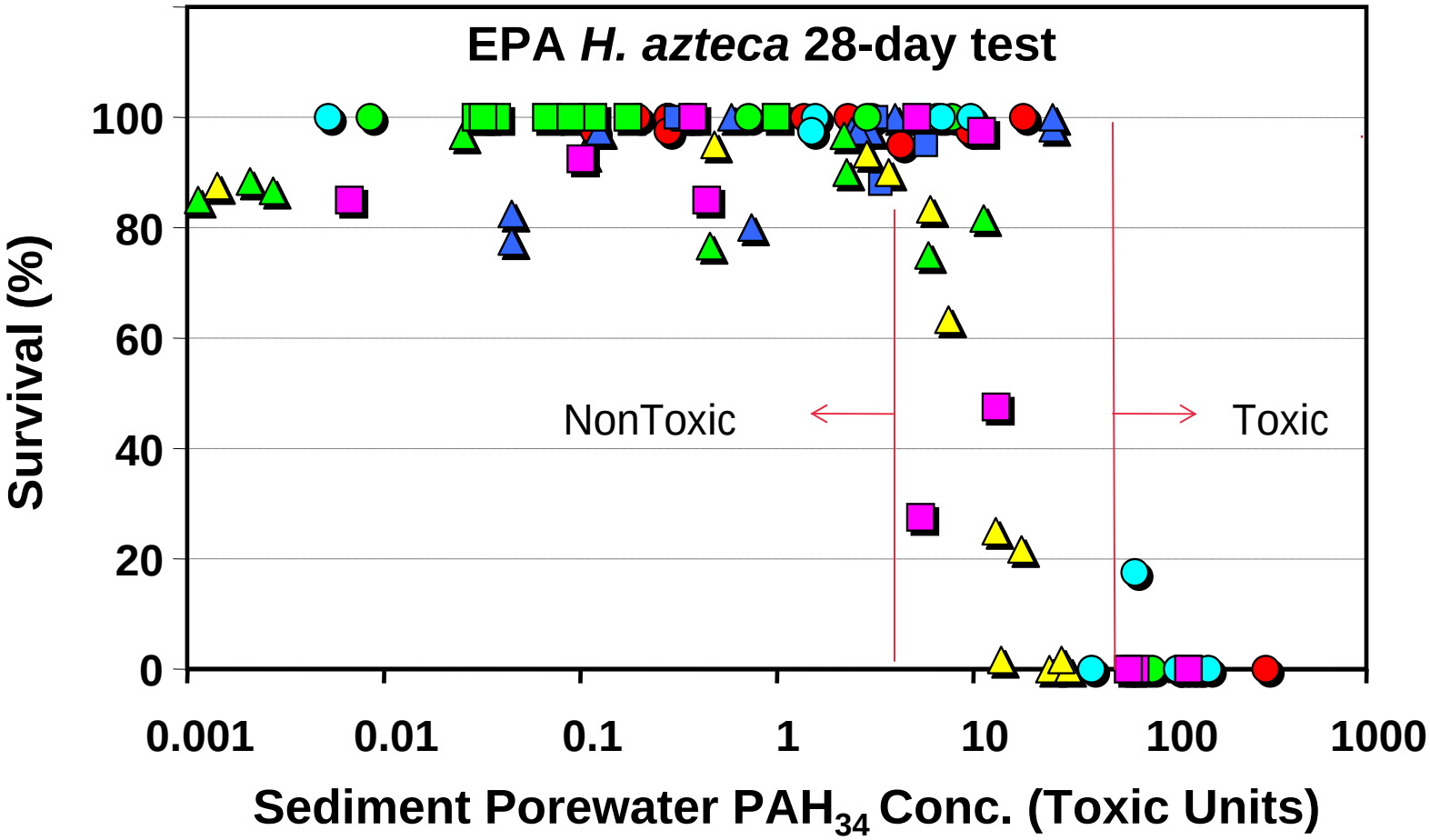
DiToro et al. 2005
(Courtesy of D Reible, U of Texas)

Bulk Solid PAH Relationship to Effect *Hyalella* survival at MGP Sites



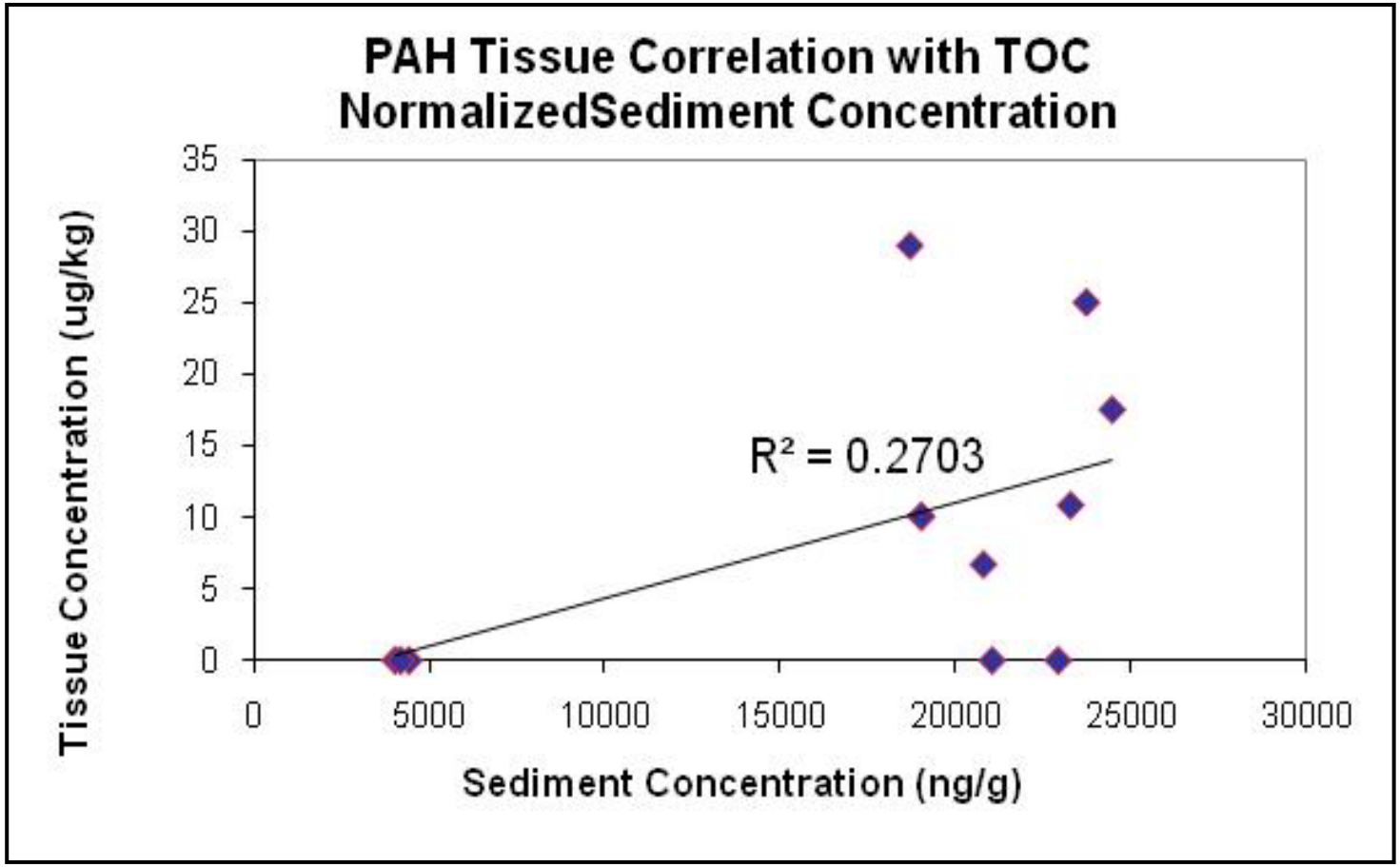
(Courtesy of Dave Nakles, Carnegie Mellon University and D Reible, U of Texas)

Porewater PAH Relationship to Effect *Hyalella* survival at MGP Sites



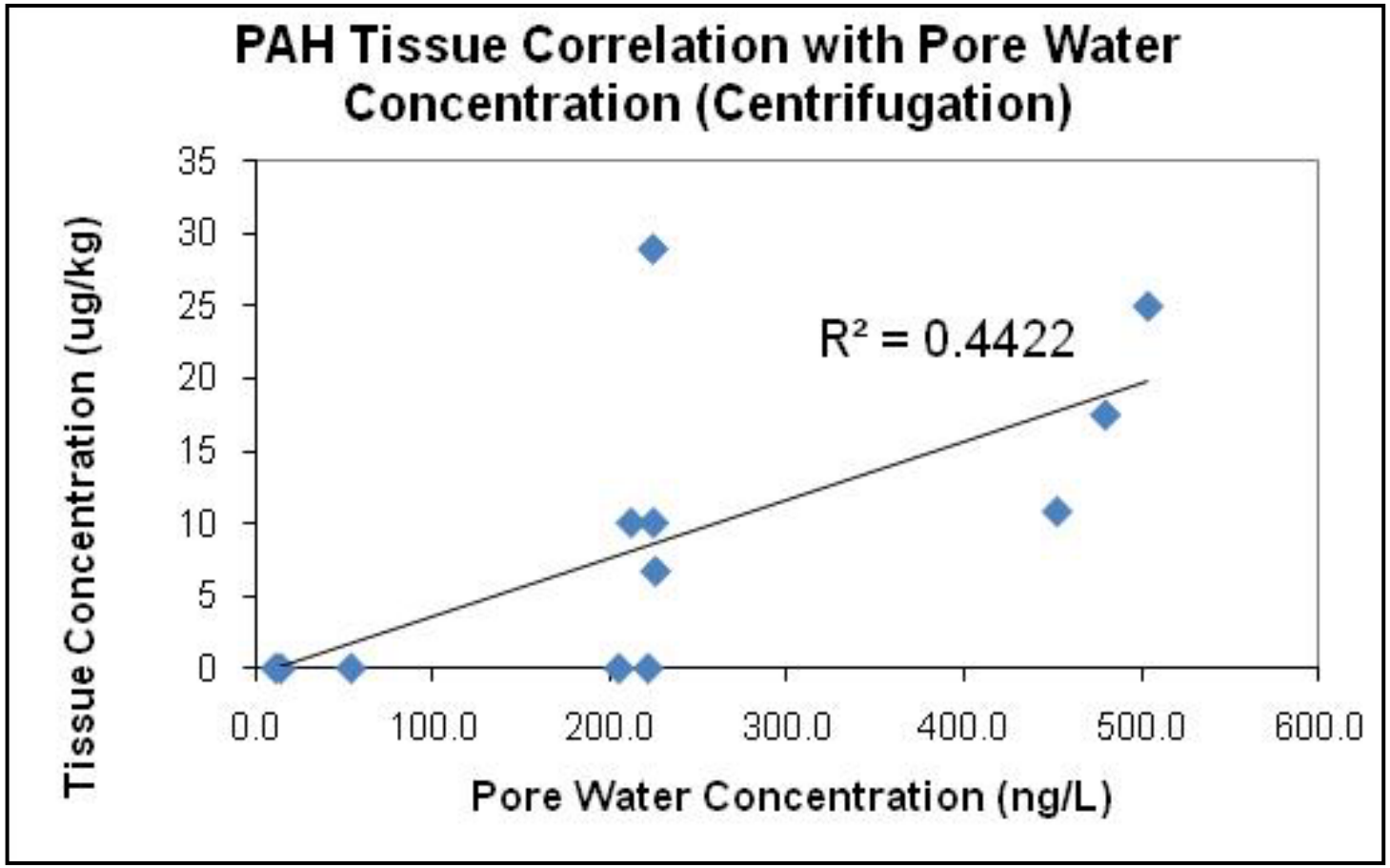
(Courtesy of Dave Nakles, Carnegie Mellon University and D Reible, U of Texas)

PAH Bioaccumulation in San Diego Harbor
B(b)F, B(k)F, B(a)P in Bivalves



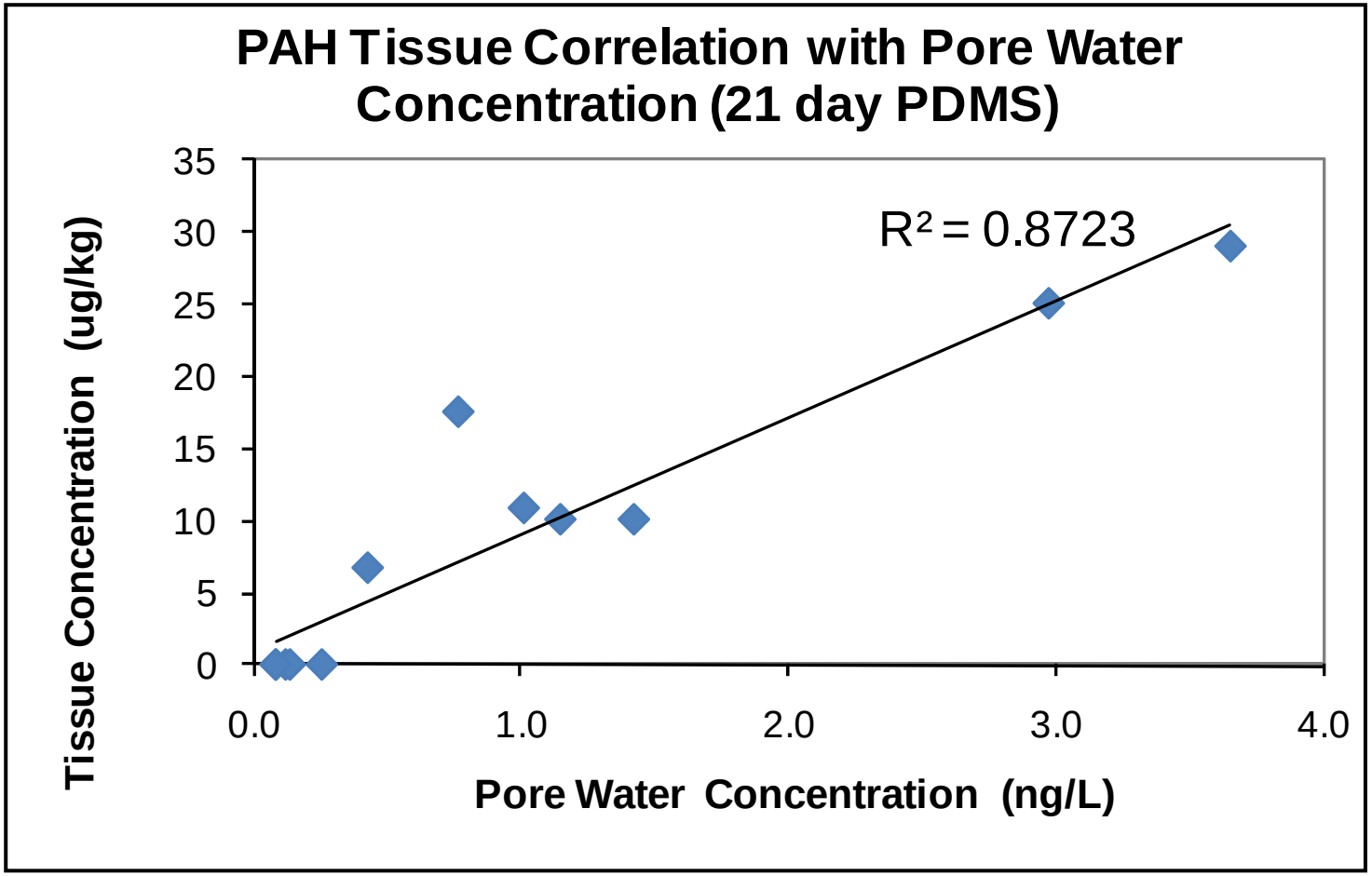
(Courtesy D Reible, U of Texas)

PAH Bioaccumulation in San Diego Harbor B(b)F, B(k)F, B(a)P in Bivalves



(Courtesy D Reible, U of Texas)

PAH Bioaccumulation in San Diego Harbor B(b)F, B(k)F, B(a)P in Bivalves



(Courtesy D Reible, U of Texas)

Presentation Outline

- Buffalo River Area of Concern
- Porewater background and scientific principals
- Derivation of PAH Remedial Goals for Buffalo River Sediment
- Other Chemicals Evaluated for Buffalo River Sediment
- Conclusions

Derivation of RG for Total PAHs

- Toxicity-based approaches
  - Equilibrium partitioning (EqP)
  - Target Lipid Model (TLM)
- Unlike empirical screening benchmarks, toxicity-based approaches account for
  - Site-specific bioavailability
  - Unique compositions of total PAH mixtures
  - Lipid content of receptor
  - Relevant species and habitat sensitivity

PAH EqP Sediment Benchmark Approach

- The approach sums the toxicological contributions of 34 PAHs to estimate a sediment benchmark protective of benthic organisms (Toxicity Unit ≤ 1) for PAH mixtures

1. Sum of PAH toxicity based on PAH mixtures

$$\Sigma\ (\text{PAH}_{\mu g/g\ OC} \div \text{Final Chronic Value}) \rightarrow \Sigma\ TU$$

2. Back calculate a sediment screening benchmark

$$\boxed{\text{Benchmark (ESB)} = \Sigma\ TU \leq 1}$$

PAH TLM Approach

- The approach assumes the toxicity of the PAH mixture is based on the sum of PAHs in the lipid fraction of an organism

- Evaluation of PAH toxicity based on TLM approach:

Σ PAH µg/g lipids ≤ **No Effect Body Residue µg/g lipids** = **Safe Sediment**

Field-measured lipid-normalized PAH concentrations

USEPA Guidance (USEPA 2003; DiToro et al. 2000)

Site-specific result

Information Evaluated in Derivation of PAH RG for Buffalo River

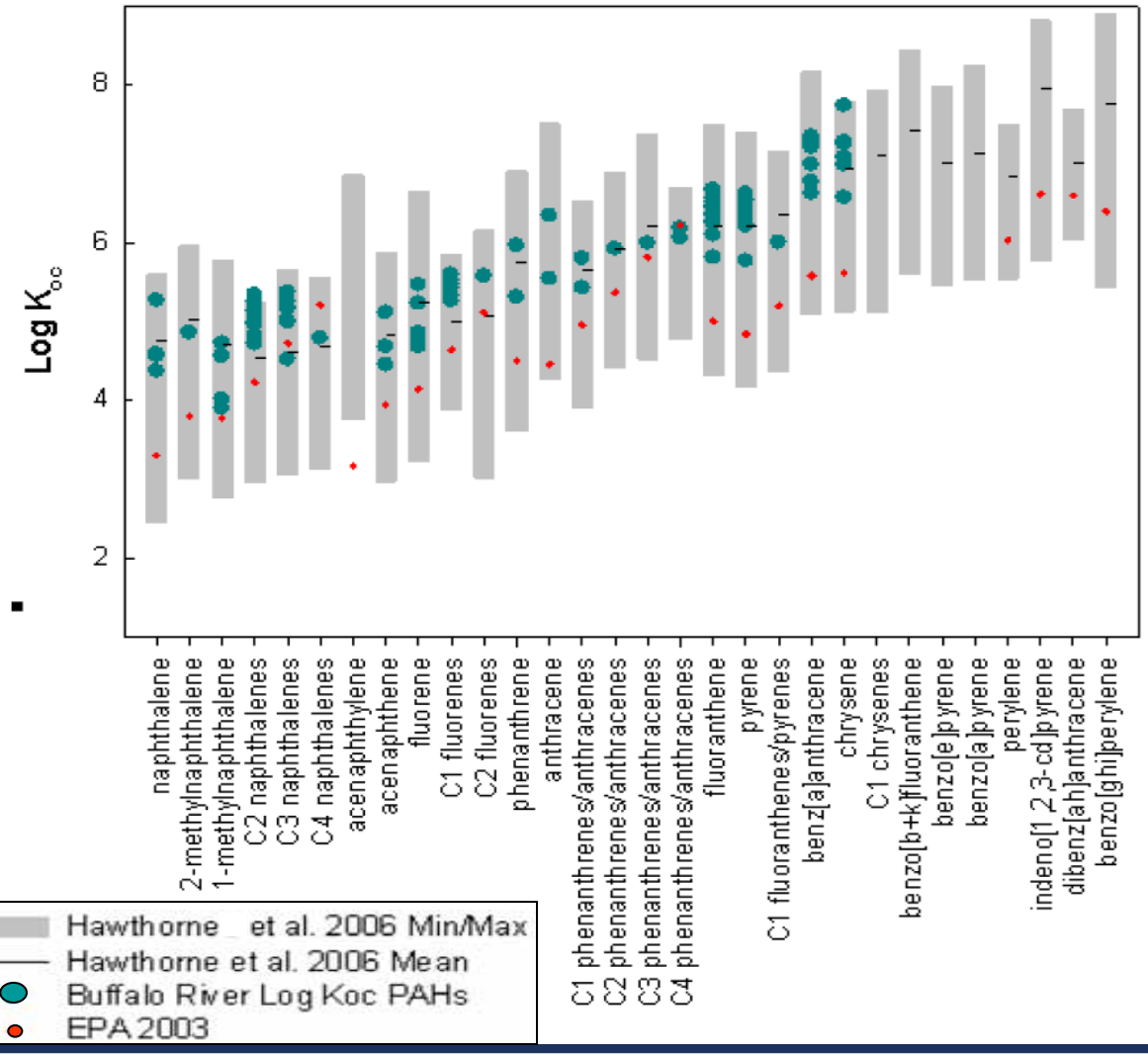
- Site-specific Parent PAHs (17 PAH compounds)
- Site-specific Parent and Alkylated PAHs
  - Developed a conversion factor between 17 and 34 PAH compounds
  - USEPA conversion factor default: 1.6 - 16.9x
  - Site-specific conversion factor: 1.36x
- TLM worm bioaccumulation evaluation
- Site-specific PAH porewater concentrations and corresponding K_{oc} values

Porewater Analysis for PAH Compounds

- Surface sediment samples were collected from 20 Buffalo River AOC locations
- Porewater was separated from sediment via centrifugation
- Porewater PAH analysis
  - Included parent and alkylated PAHs
  - Compounds were measured using solid-phase microextraction (SPMD) followed by GC/MS (ASTM D7363)
  - Parent and alkylated PAHs were measured in whole sediment samples
  - Calculated K_{oc} values

$$K_{OC}\ (L/g) = \frac{\text{Whole Sed PAH Conc (mg/kg)}}{\text{Porewater PAH Conc (mg/L)} \cdot \text{TOC (\%)}} \cdot \frac{\text{kg}}{1000\ \text{g}}$$

Log K_{oc} Values for PAH Compounds in Sediment



- Buffalo River values fall within the range of experimentally-determined values
- Buffalo River values are typically higher than the values derived by USEPA's default values
- Buffalo River values indicate greater partitioning to sediments than predicted by the USEPA model

PAH EqP and TLM Results

- TU and RG Derivation Results

Data Set	TUs	Total PAH RG (as Σ 17 PAHs)
Unbounded no effect toxicity tests	= 1	16.4 mg/kg
Sediment toxicity tests w/ toxicity observed	<< 1 to 5 (~80% < 1)	14.5 to 26.6 mg/kg
Bioaccumulation tests	<< 1 to 2	18.2 to 43.8 mg/kg
Toxicity test with low TOC	< 1	12.4 to 15.6 mg/kg
Final selected RG	**= 1**	**16 mg/kg**

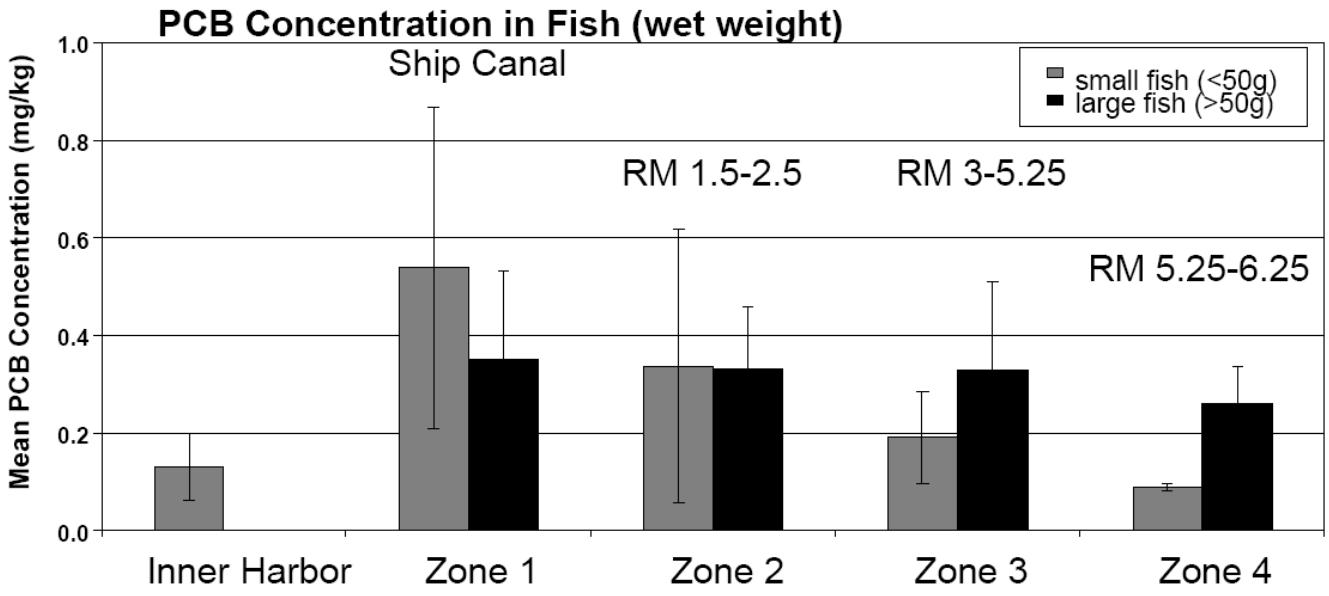
- Site-specific porewater K_{oc} values demonstrate a total PAH RG of 16 mg/kg is highly protective

Presentation Outline

- Buffalo River Area of Concern
- Porewater background and scientific principals
- Derivation of PAH Remedial Goals for Buffalo River Sediment
- Other Chemicals Evaluated for Buffalo River Sediment
  - PCBs
  - Lead
  - Mercury
- Conclusions

Development of a Risk-Based Site-Specific Remedial Goal for Total PCBs

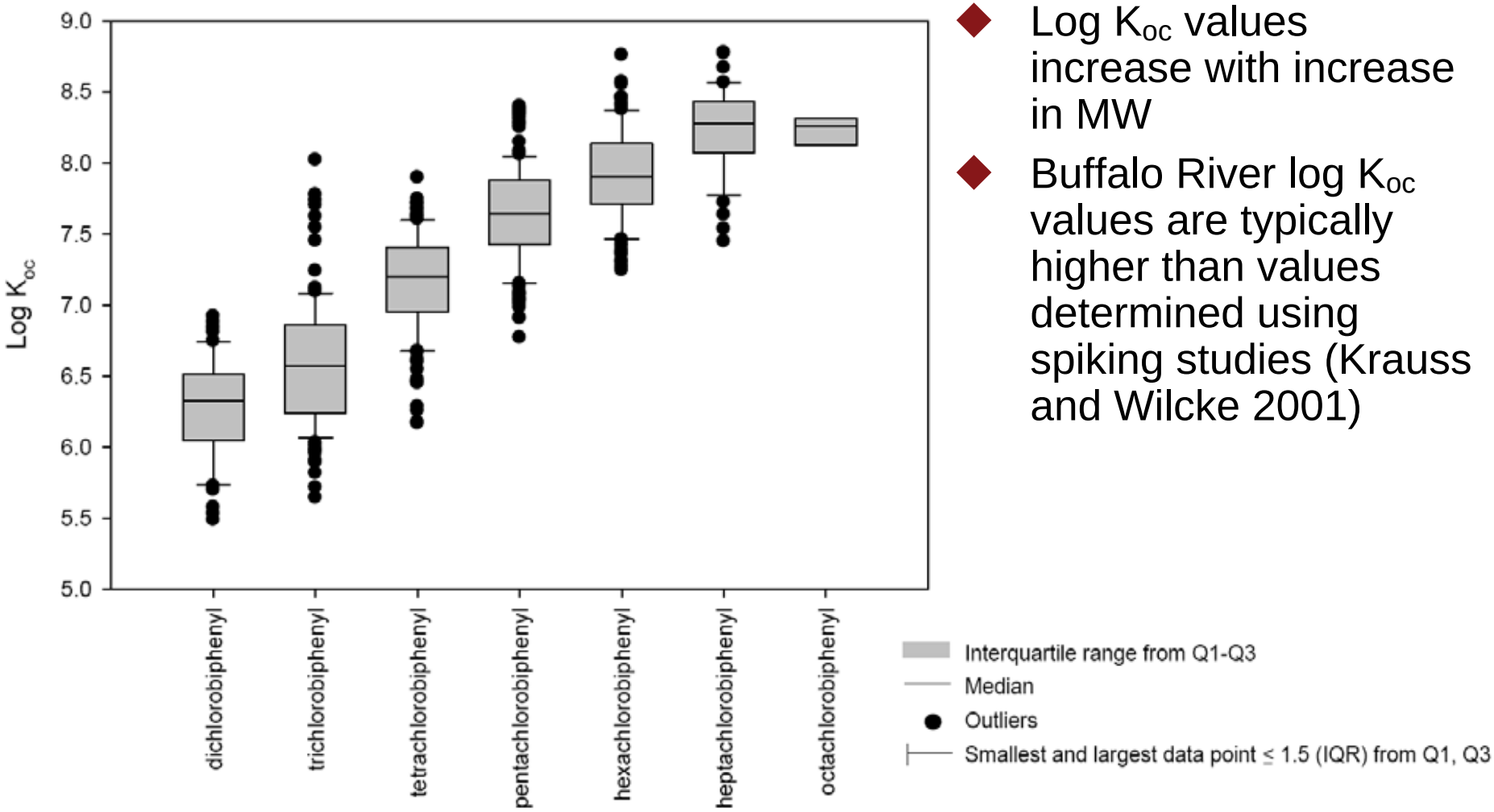
- Evaluated biological exposures to establish HQ ≤ 1 for the most sensitive wildlife receptor, the mink
- Theoretical and site-specific fish tissue concentrations used to calculate the sediment RG



Porewater Analysis for PCB Congeners

- Collected 20 surface sediment samples
- Porewater was separated from sediment via centrifugation
- Porewater PCB congener analysis
  - Concentrations determined through polyoxymethylene (POM) passive samplers
  - K_{POM} is first determined for each congener and then used to calculate PCB concentrations in porewater

Log K_{oc} Values for PCB Homologs in Buffalo River Sediment



- Log K_{oc} values increase with increase in MW
- Buffalo River log K_{oc} values are typically higher than values determined using spiking studies (Krauss and Wilcke 2001)

Site-Specific Remedial Goal for Total PCBs

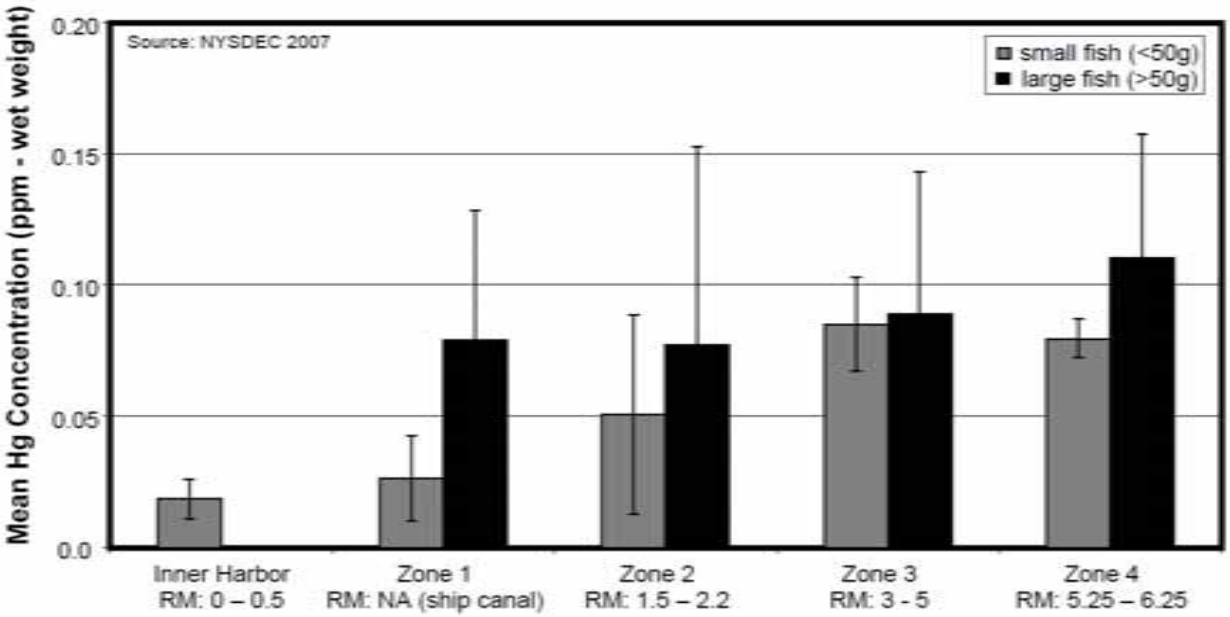
- Results from the multiple lines of evidence demonstrate total PCB sediment concentrations ranging 0.18 - 0.44 mg/kg are protective of fish and piscivorous wildlife
- The RG for total PCBs is a SWAC of 0.20 mg/kg

Development of a Site-Specific Remedial Goal for Lead

- Evaluated multiple lines of evidence
  - Sediment toxicity tests
  - Lead sediment concentrations, 95% UCL
  - Risk-based evaluation of fish ingestion by mink
  - Risk-based evaluation of fish ingestion by kingfisher
  - Risk-based evaluation of worm and sediment ingestion by ducks
- Current conditions do not pose risks
- RG was determined to provide a standard for post-remedy conditions

Development of a Site-Specific Remedial Goal for Mercury

- Multiple lines of evidence were evaluated
  - Mercury fish tissue concentrations
  - Sediment toxicity tests
  - Mercury sediment concentrations, 95% UCL
- Current conditions do not pose risks
- RG provides a standard for post-remedy conditions



Presentation Outline

- Buffalo River Area of Concern
- Porewater background and scientific principals
- Derivation of PAH Remedial Goals for Buffalo River Sediment
- Other Chemicals Evaluated for Buffalo River Sediment
- Conclusions

Conclusions

- Porewater chemical concentrations are much more strongly correlated with effects compared to whole sediment concentrations
- Porewater analytical methods are well established in published literature
- Porewater measurements combined with whole sediment samples provide an opportunity to develop site-specific K_{oc} values
  - Equilibrium partitioning models
  - Bioaccumulation models (e.g., Gobas-based models)
  - Default K_{oc} values can significantly over- or underestimate risk
- Risk-based decisions should rely on multiple lines of evidence, focusing primarily on site-specific data