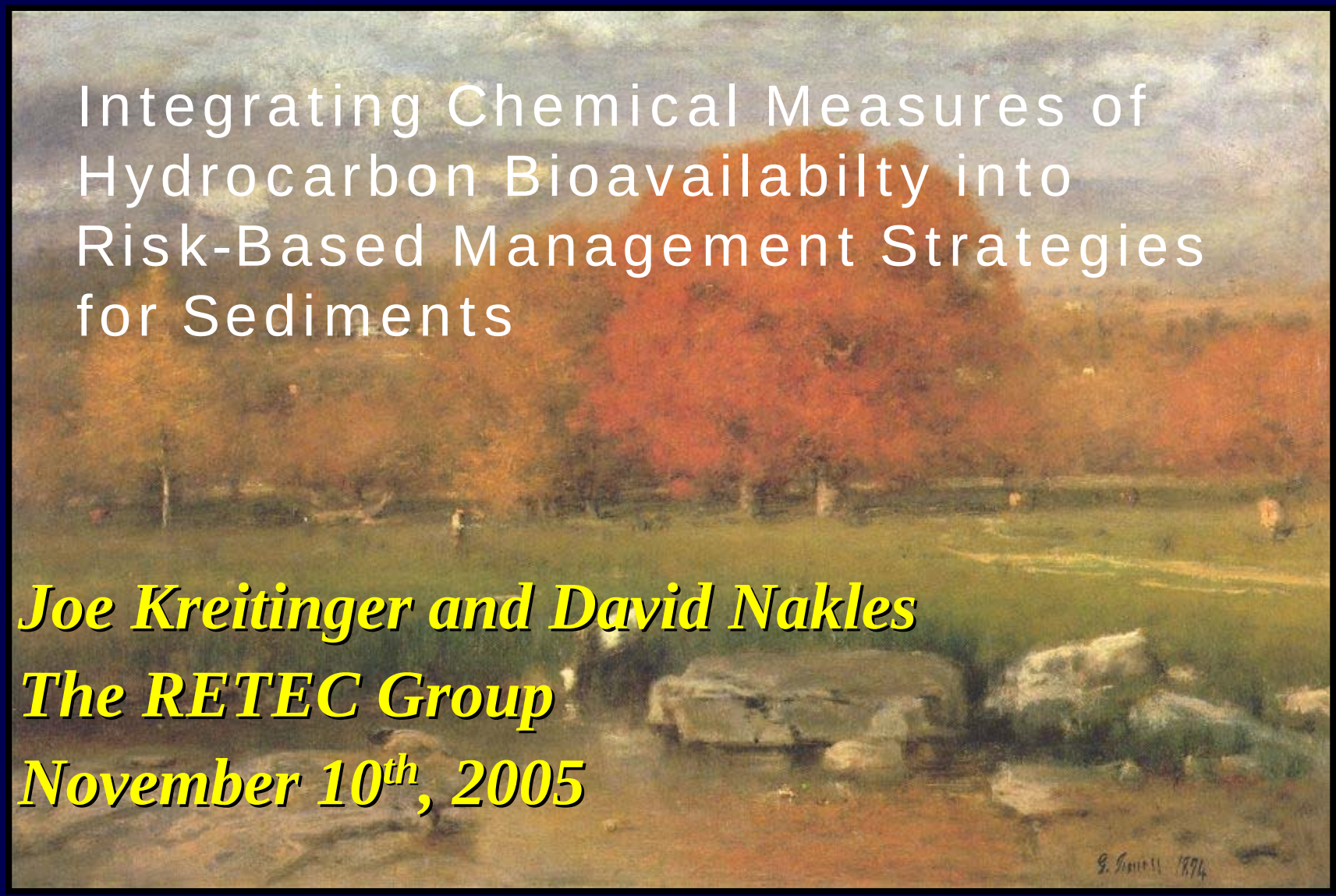
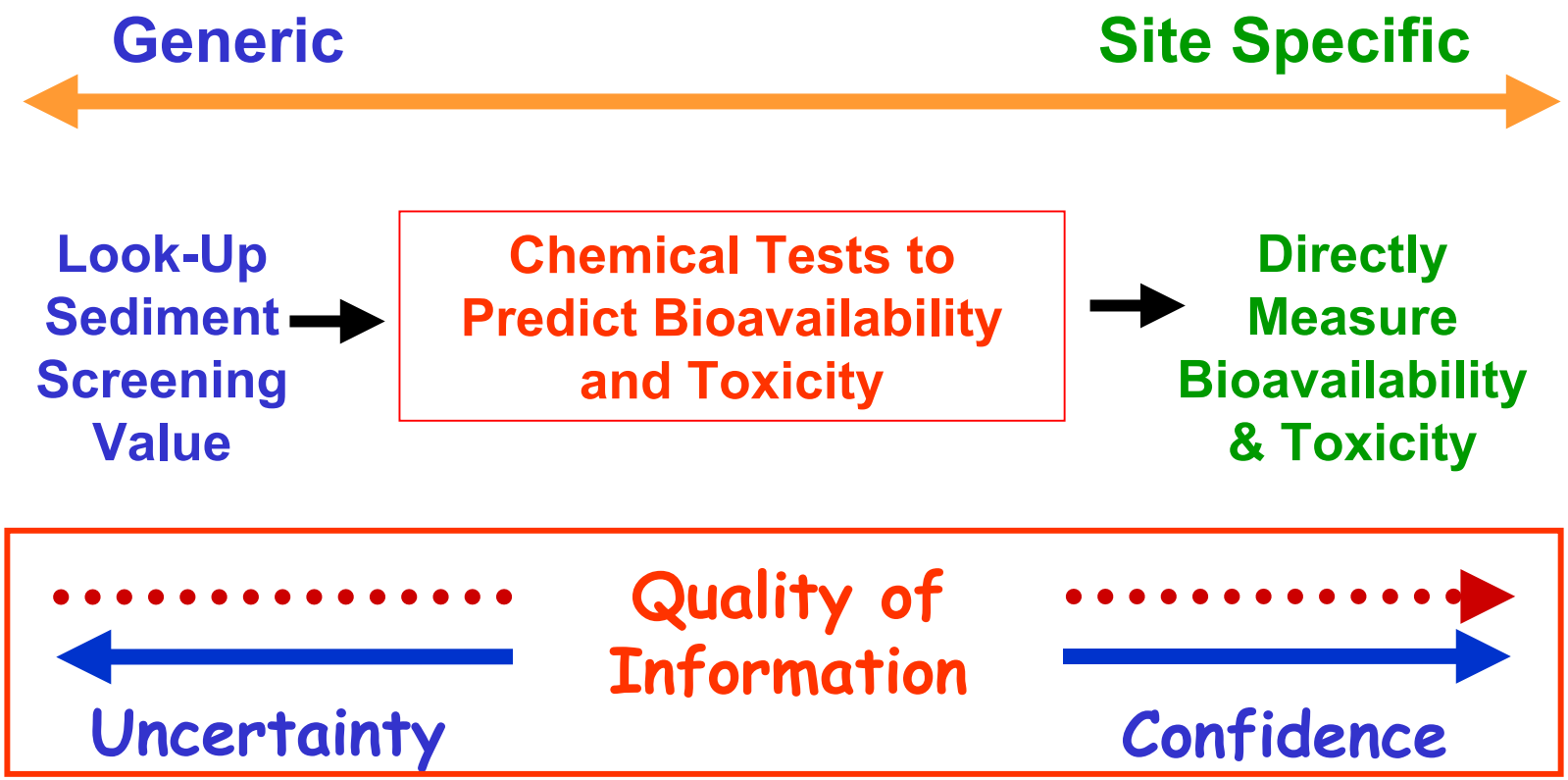
Integrating Chemical Measures of Hydrocarbon Bioavailabilty into Risk-Based Management Strategies for Sediments



Joe Kreitinger and David Nakles
The RETEC Group
November 10th, 2005

Can We Improve Technical Framework for Sediment Management?



Value of Improving Chemical Predictors of Sediment Toxicity

- **Better information for remedial decision-making**
  - **Prioritize where resources are spent**
  - **Expedite site closures**
  - **Reduce costs**
- **More focused monitoring methods**
  - **Residuals following dredging**
  - **Long-term monitoring of caps**
  - **MNA evaluation**

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Assessing the Bioavailability of PAHs in Soils and Sediments

How did we get here?

- **Gas Research Institute: bioavailability research initiated in 1993**
  - **Published "Red Book"**
  - **Petroleum Environmental Research Forum study followed**
  - **Conclusion: Bioavailability is important concept but more carefully integrated studies were needed**
- **Two follow-on industry supported research programs initiated in 1997:**
  - **CA human health study: Lampblack-impacted soils ($1MM)**
  - **NY ecological study: PAH-impacted soils/sediments (~ $3 MM)**

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Significant Collaborative Research with Academic and National Laboratories

Characterizing bioavailability and toxicity of PAHs in MGP site soils/sediments since 1993

- The RETEC Group (Ithaca, NY; Pittsburgh, PA)
- Gas Research Institute (Chicago, IL)
- Lawrence Berkeley National Laboratory (Berkeley, CA)
- Cornell University (Ithaca, NY)
- Stanford University (Palo Alto, CA)
- University of Texas (Austin, TX)
- University of North Dakota (Grand Forks, ND)
- Ohio State University (Columbus, OH)
- University of Maryland, (Baltimore, MD)
- US Army Engineering Research & Development Center

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Approaches for Assessing Bioavailability

- ***Characterize carbon-types and assign carbon-specific partitioning coefficients?***
- **Determine sediment pore water chemical concentrations**
- **Use direct measurements of chemical release to predict bioavailability**
- **Directly measure uptake and toxicity to organisms directly**

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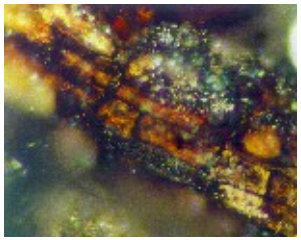
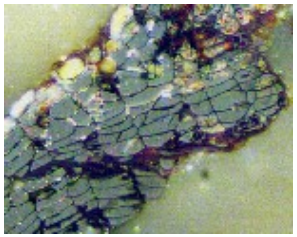
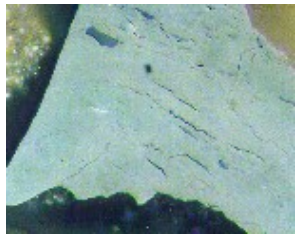
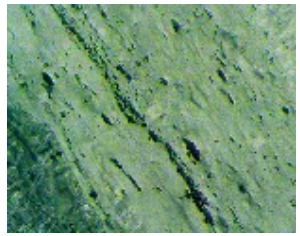
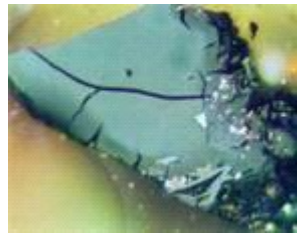
Survey of Hudson River Sediments Demonstrated Presence of Natural and Anthropogenic Carbon

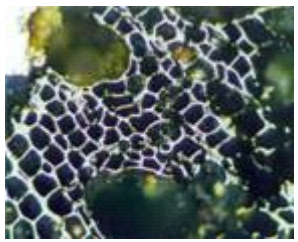

wood

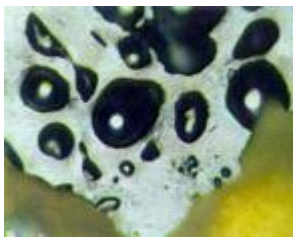

lignite

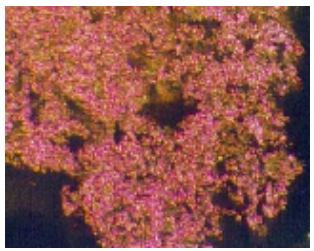

bituminous coal

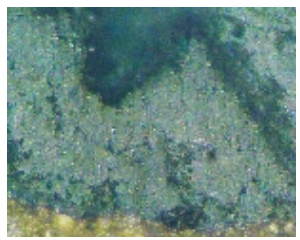

anthracite coal

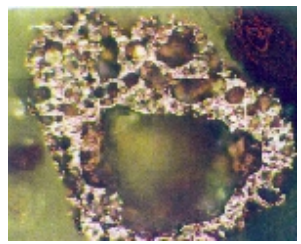

oxidized coal


charcoal


coke


soot carbon


coal tar pitch


cenosphere

PAH binding (Koc) is very different for different types of carbon

(U. Ghosh et al. , 2003)

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Two Chemical Methods have been Developed and Evaluated

- **Solid Phase Micro Extraction (SPME)**
  - **Measures the dissolved concentration of PAHs in sediment pore water**

- **Supercritical Fluid Extraction (SFE)**
  - **Measures the release of PAHs in sediment samples**

Do these measurements correlate to bioavailability?

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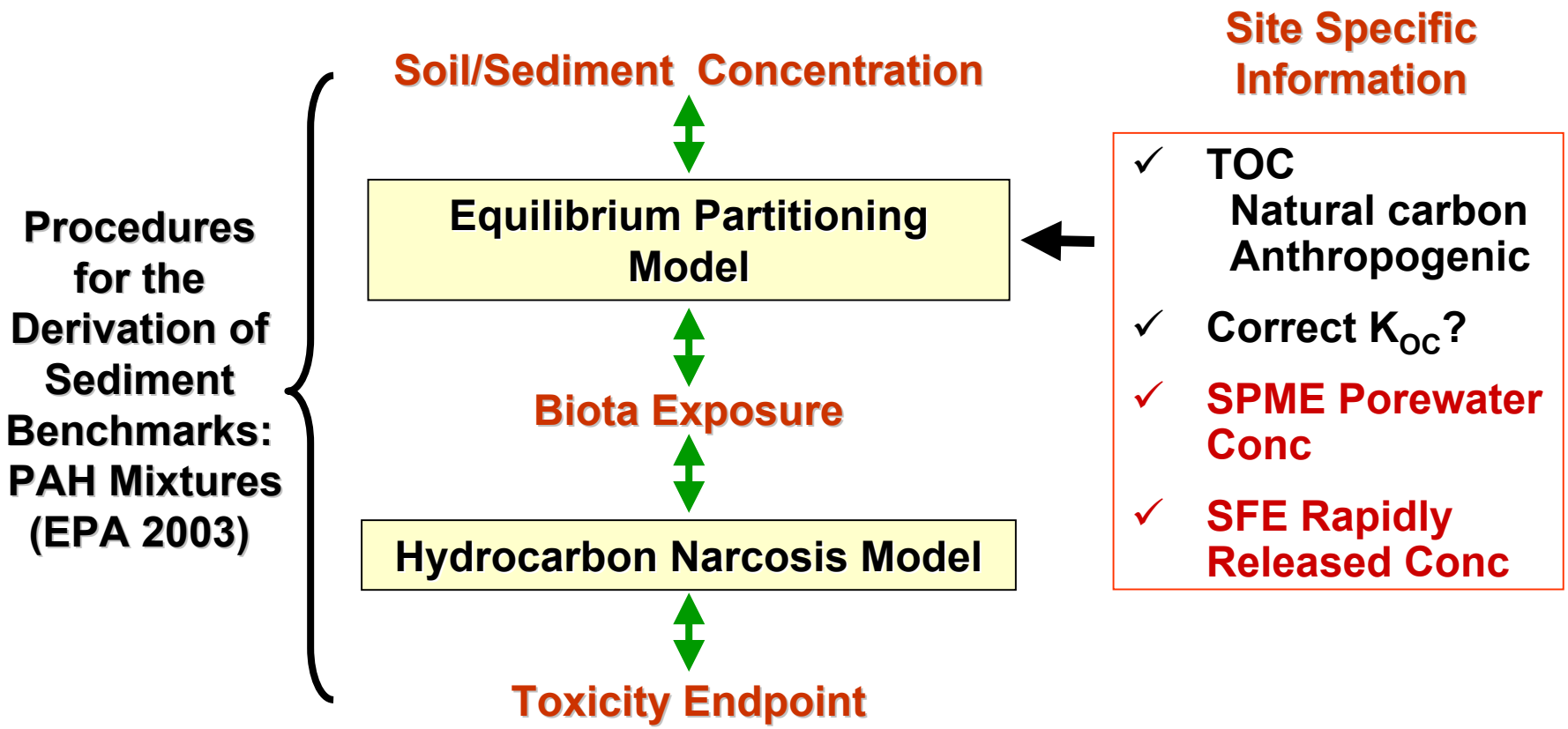
Site Specific Measures Of Chemical Availability Reduce Uncertainty In Predicting Exposure



Solid Phase Microextraction (SPME) of Pore Water

- ✓ **Uses sorbent microfiber**
- ✓ **Accurately measures PAHs in pore water**
- ✓ **Rapid – 30 minutes**
- ✓ **Small sample size required**
  - **~ 20 ml of sediment**
  - **~ 1.5 ml of pore water**
- ✓ **Very low detection limit**
  - **~ pg/mL (ppt)**

(Hawthorne et al., 2005b)

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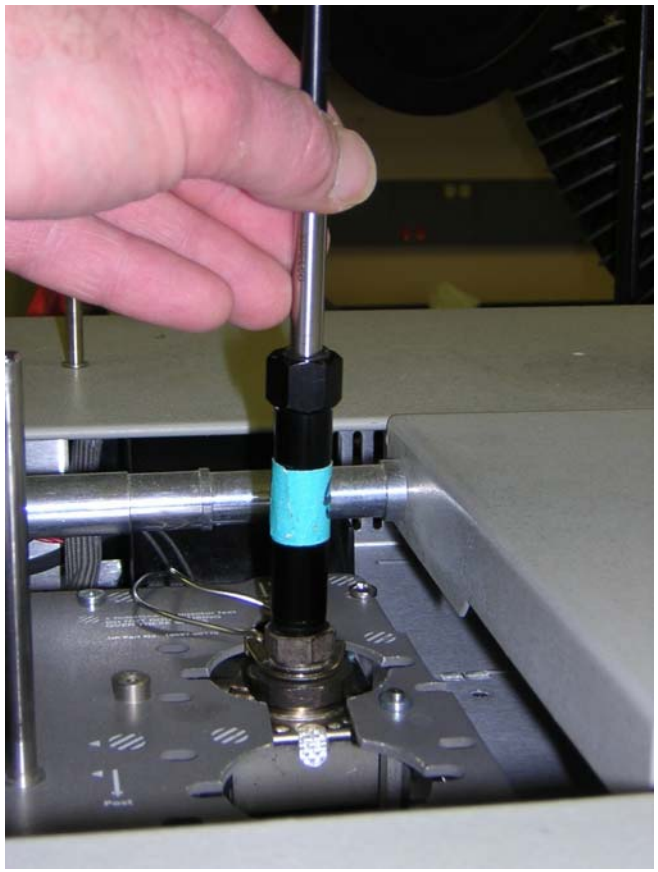
SPME Fiber Injection into GC/MS



Conventional EPA water analysis methods would require liter(s) of sediment pore water to achieve similar sensitivity

Detection limits for representative PAHs

	EPA 8270 EQL 1 liter water	SPME 1.5 ml water
Naphthalene (2-ring)	10 μg/l	0.5 μg/l
Phenanthrene (3-ring)	10	0.2
Chrysene (4-ring)	10	0.01
Benzo(a)pyrene (5-ring)	10	0.005
Benzo(g,h,i)perylene (6-ring)	10	0.002

Why is SPME so much more sensitive for larger PAHs?

All molecules collected by SPME are transferred to the GC

For 8270 only ca. 0.1% are injected

(Hawthorne et al. , 2005b)

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Supercritical Fluid Extraction (SFE) of Sediments

- **Extraction Conditions**
  - ✓ **Liquid CO_2,200 atmos, 50°C**
  - ✓ **40 minutes extraction**
- **Advantages**
  - ✓ **CO_2 polarity is similar to lipids**
  - ✓ **Release rates correlate to water desorption**
  - ✓ **Solubility of PAHs in CO_2 is proportional to their solubility in water**
  - ✓ **Little effect on OM matrix**
  - ✓ **Can be easily calibrated to biological uptake**

(Hawthorne, 2002)

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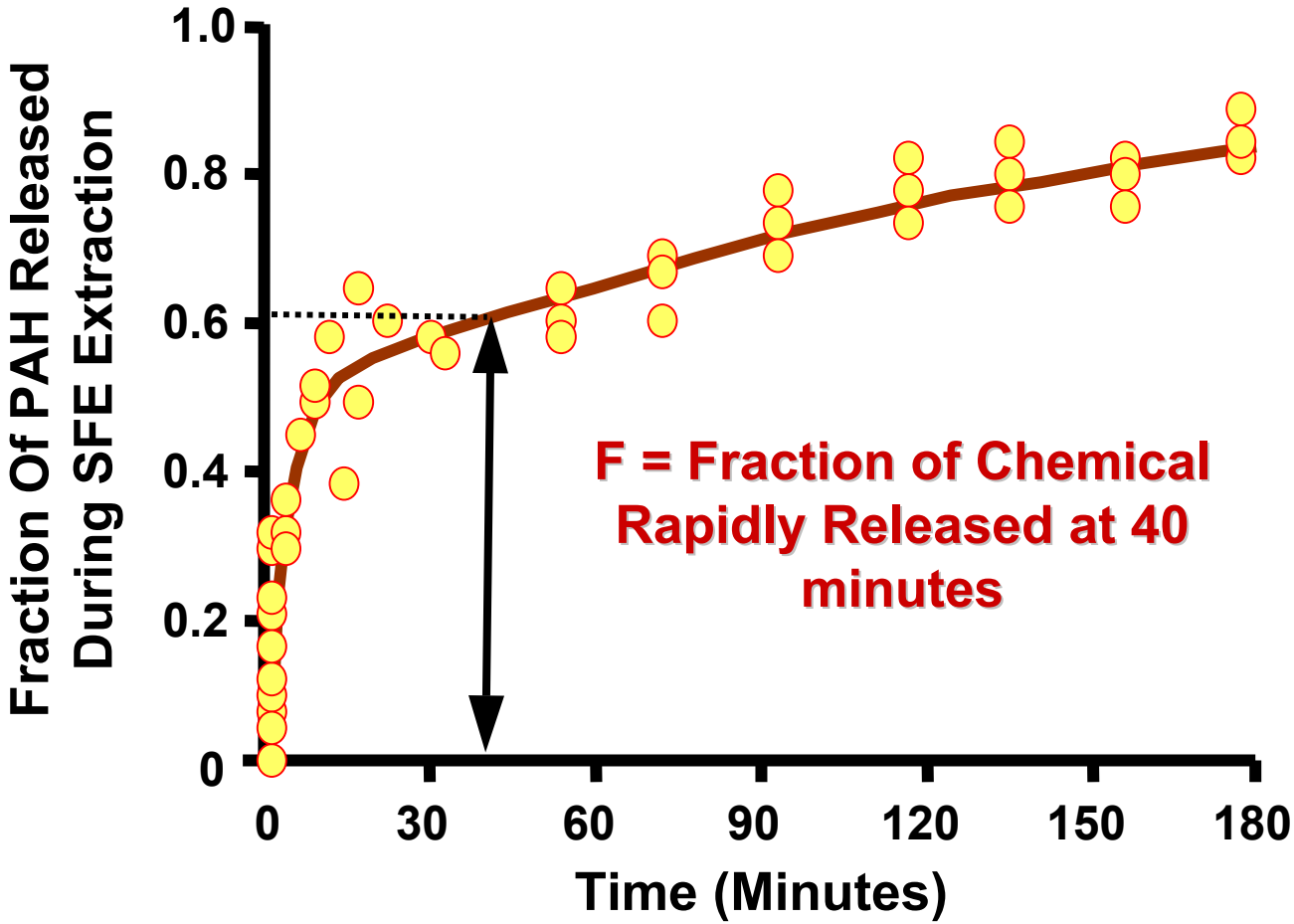
Illustrative SFE Release Curve for PAHs



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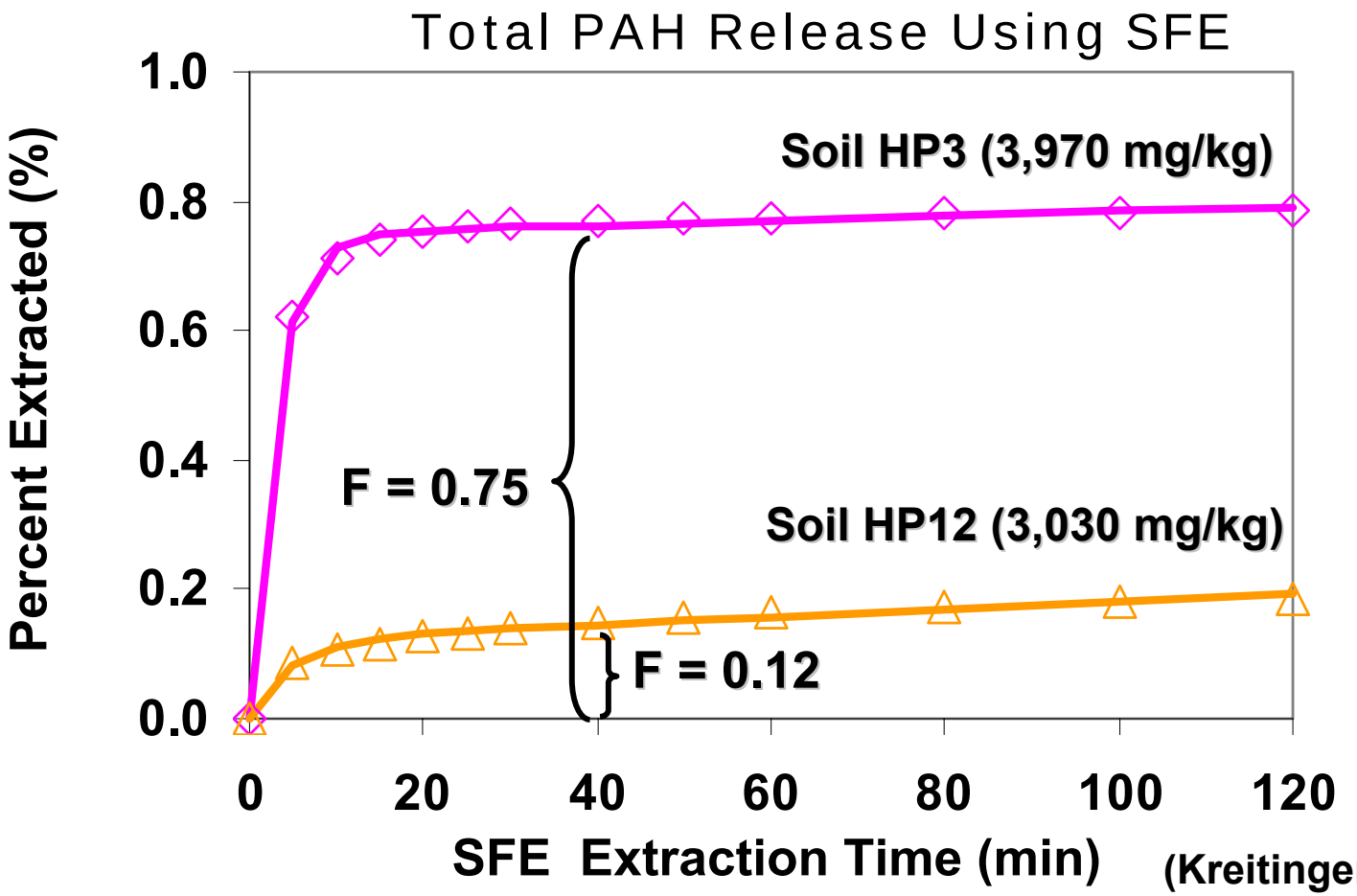
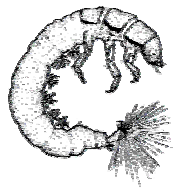
Rapidly Released Fraction (F) can Vary Significantly Between Samples

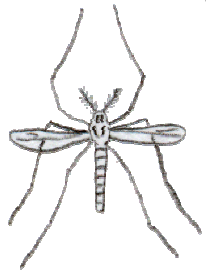


(Kreitinger et al. 2005)

Field Surveys and Case Studies to Assess Tools for Predict Bioavailability

Hyalella azteca
28-day chronic toxicity





Chironomus tentans
10-day acute toxicity

Cooperative Research and Development Agreement (CRADA)
U.S. Army Corps of Engineers
Center for Contaminated Sediments

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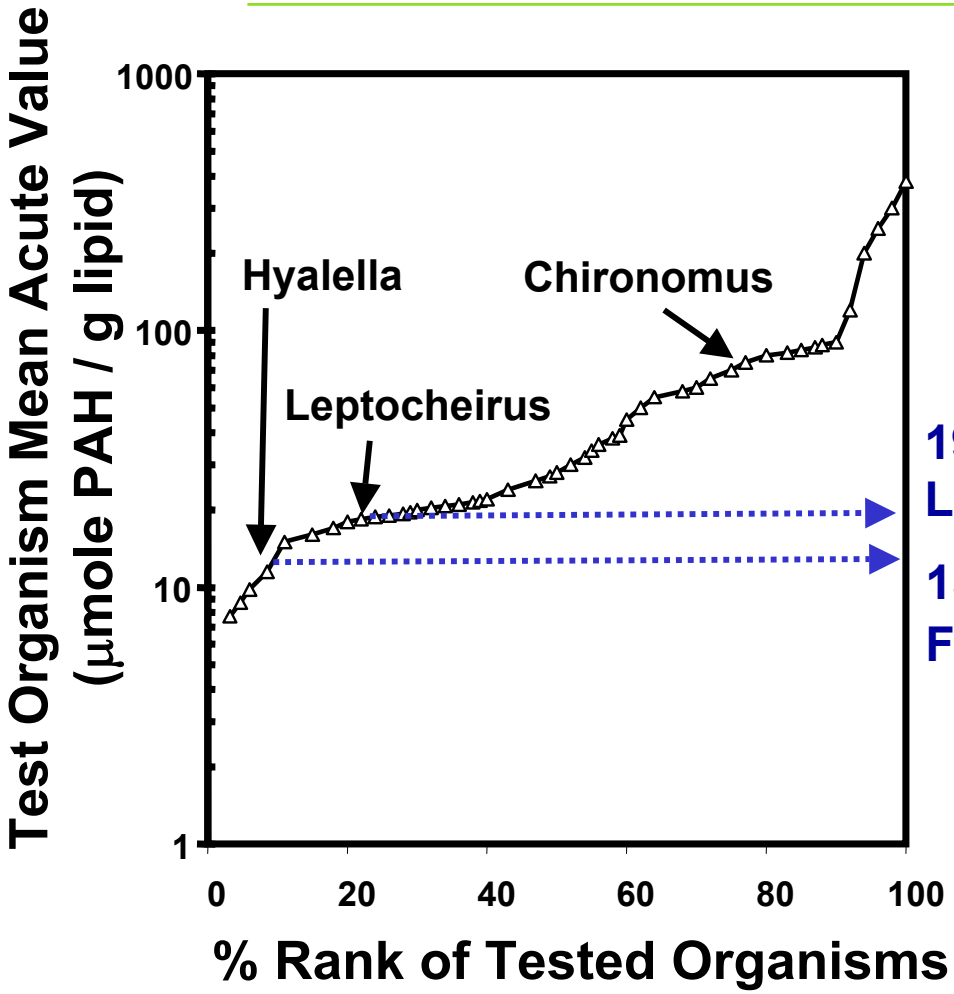
Generic Assessment Protocol Using Amphipods as Standard Sensitive Test Organisms



19.0 μmole/g lipid is toxic to Leptocheirus – Marine test species

13.9 μmole/g lipid is toxic to Hyalella – Freshwater test species

(EPA 2003)

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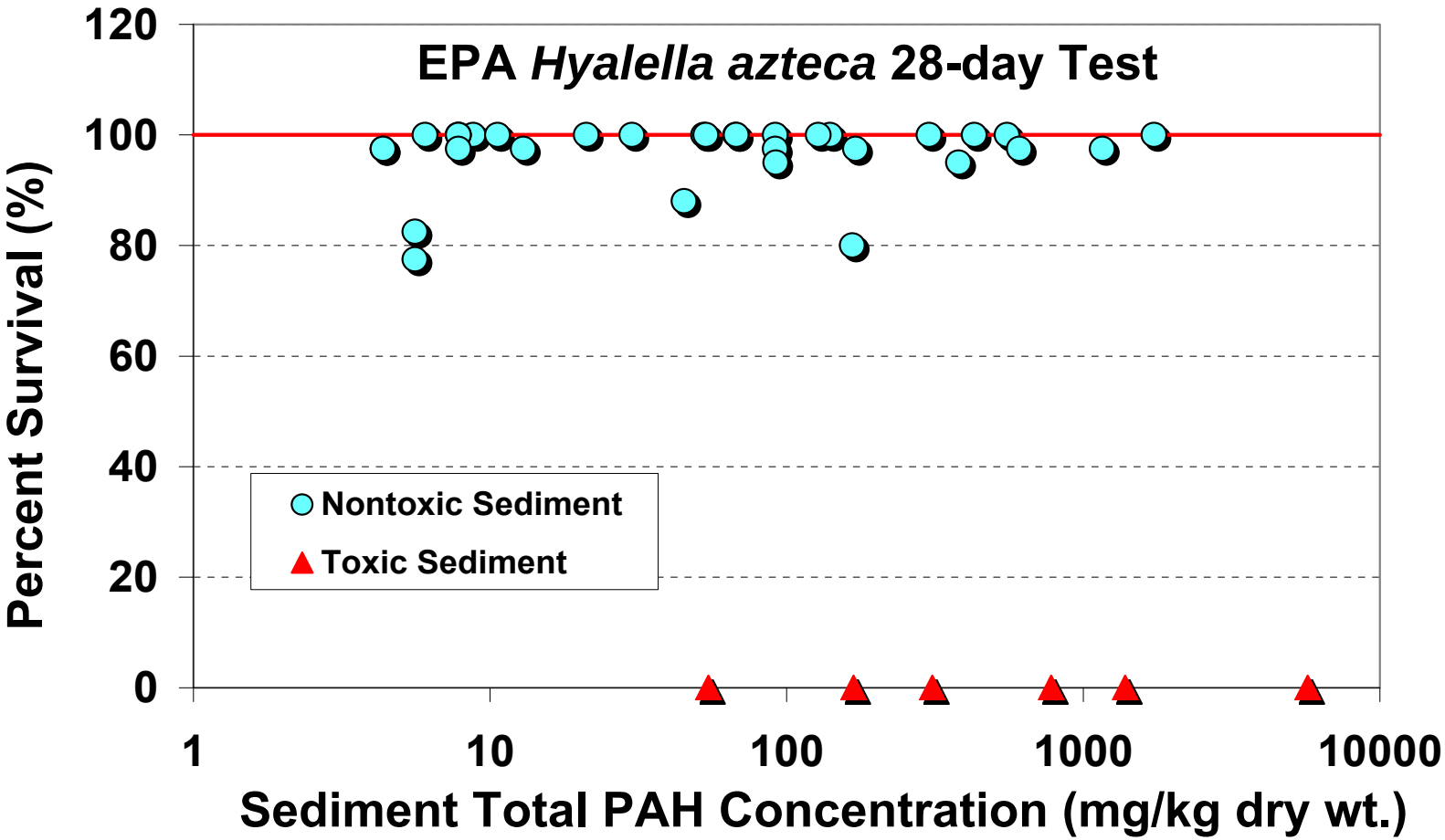
There is No Relationship Between [PAH] and Toxicity in MGP Site Sediments



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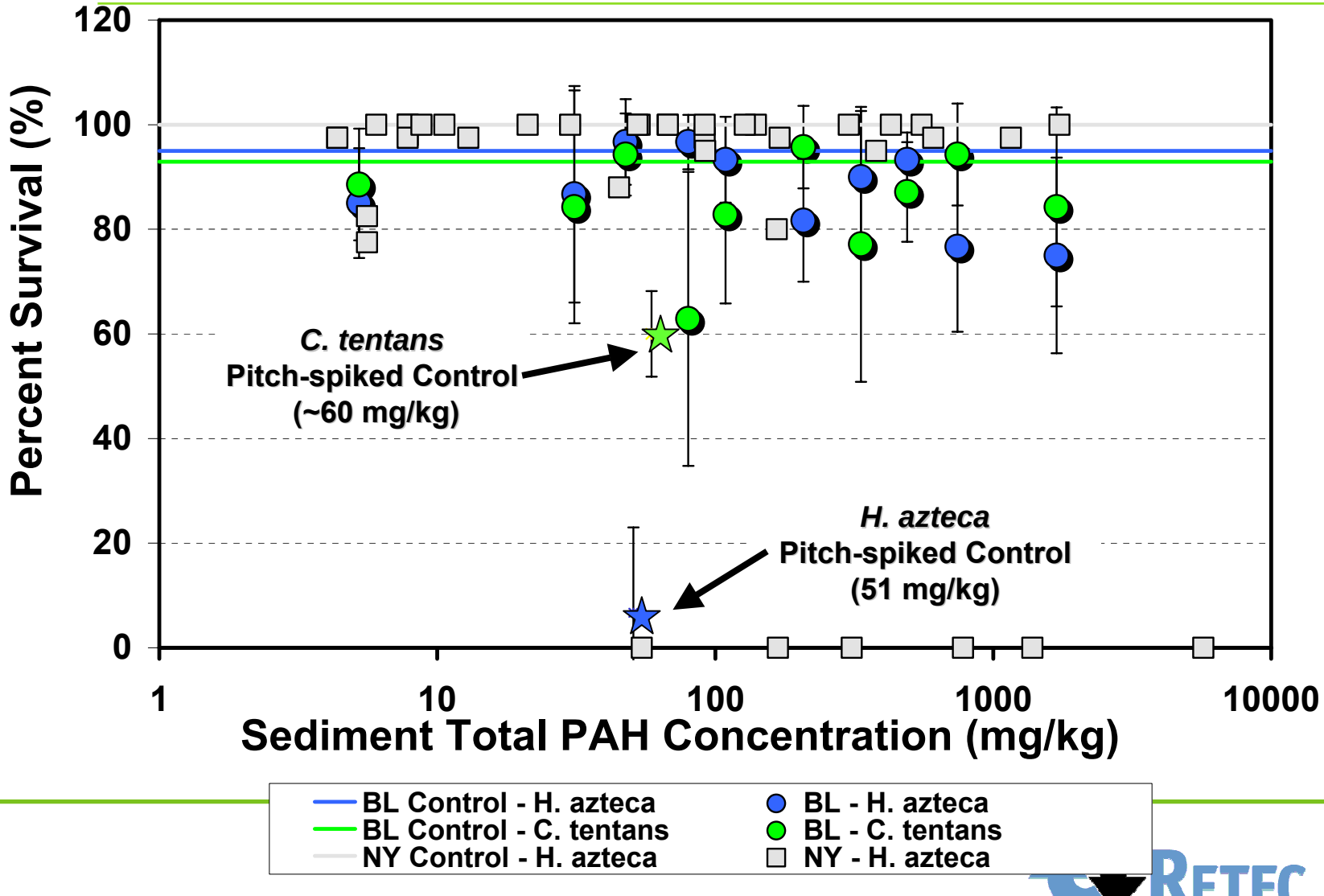
High total PAHs did not exhibit toxicity to *H. azteca* or *C. tentans* at an Aluminum Smelter Site



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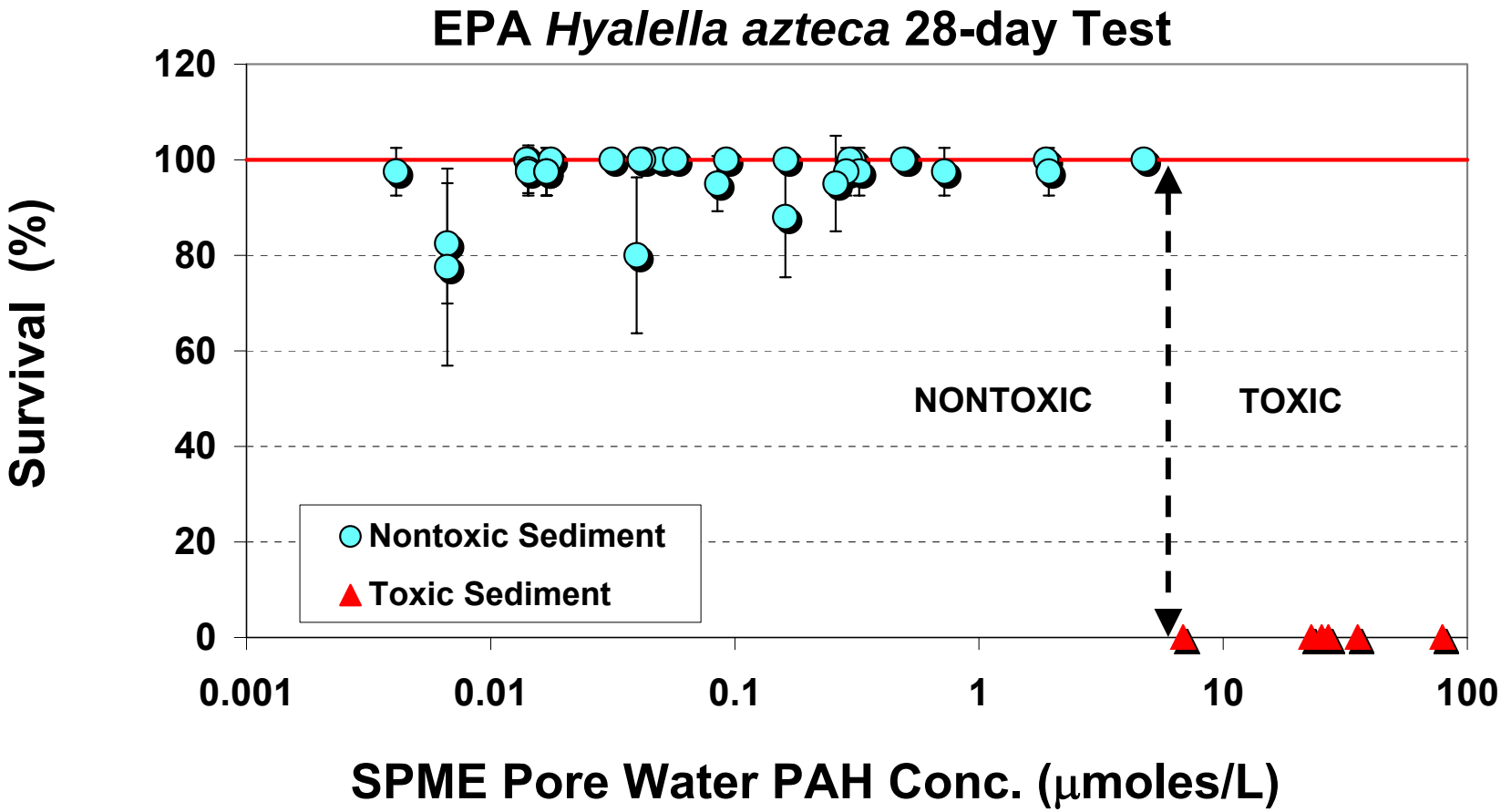
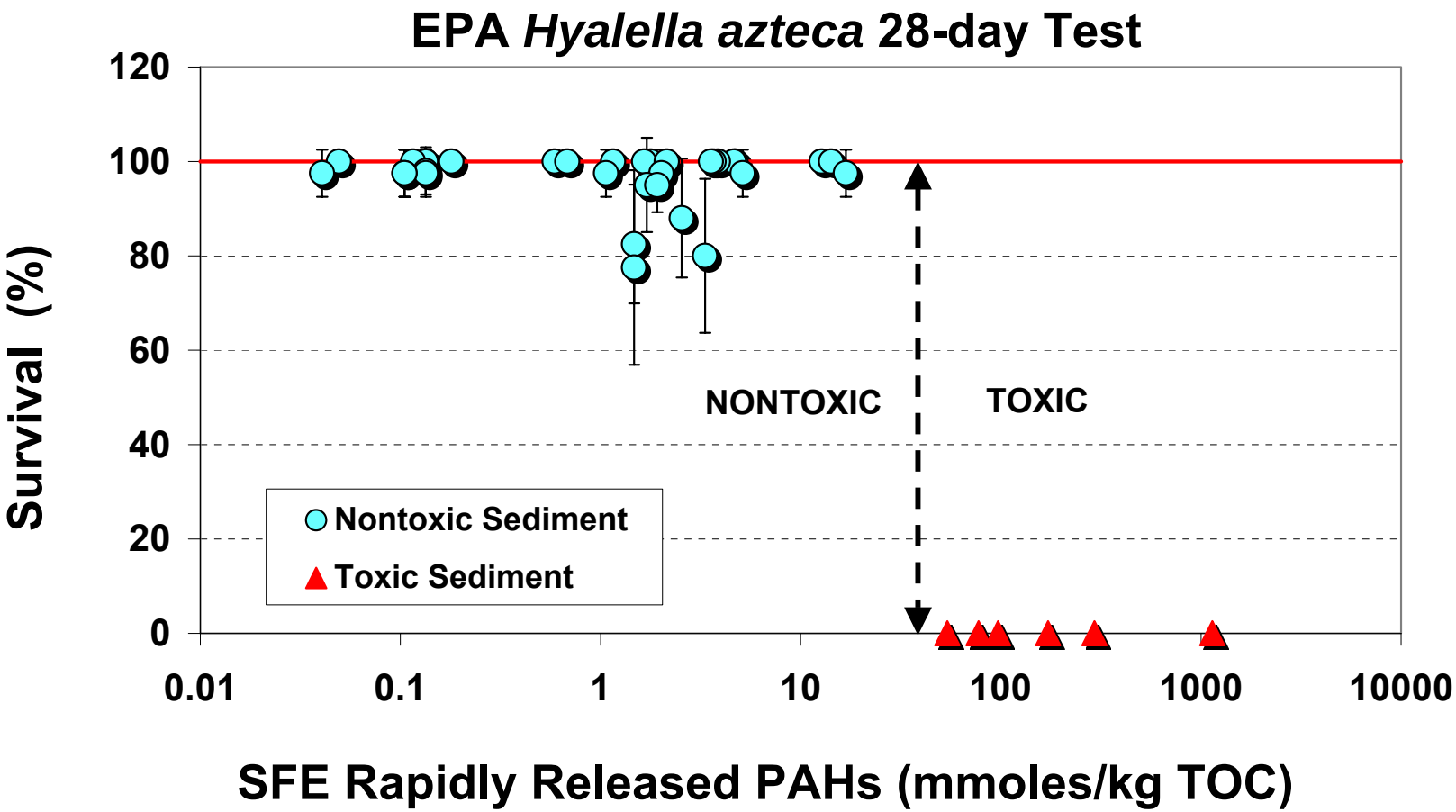
Toxicity to *H. azteca* Can be Predicted by Estimating PAHs in Porewater



Toxicity to *H. azteca* Can be Predicted by Estimating SFE Rapidly Released PAHs



Integration Within Risk-Based Decision Making

- **Use Simple Screening Tools:**
  - **To focus toxicity testing**
  - **Appropriate for the size of the problem**
- **Implement Case-Studies:**
  - **Assure appropriate toxicity endpoints**
  - **Gain regulatory acceptance**

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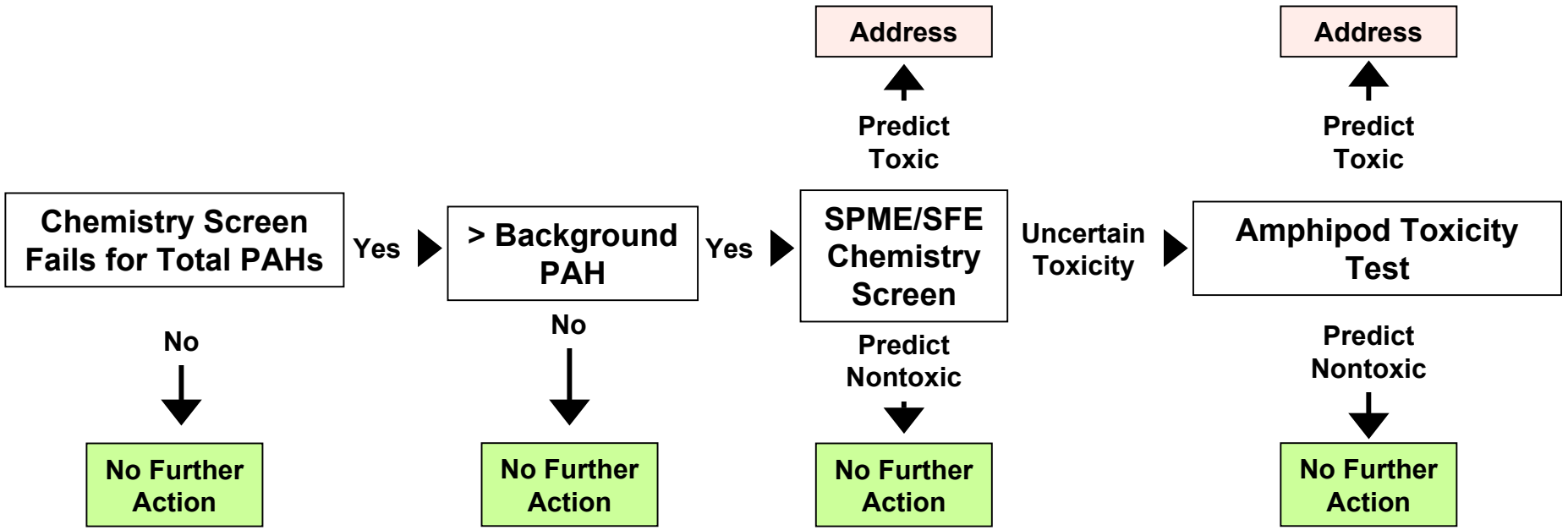
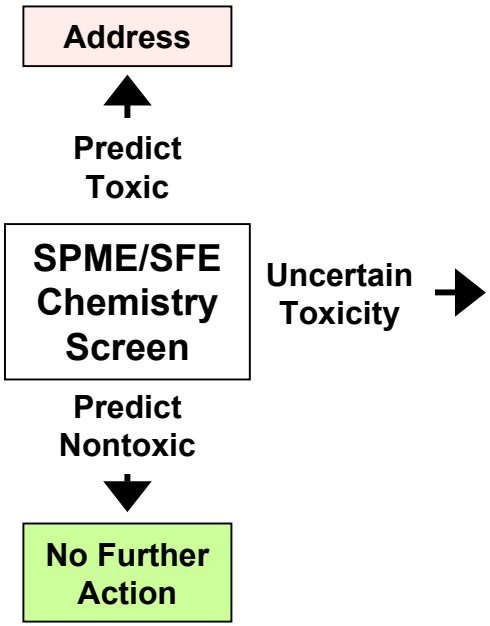
1. Anticipated Approach Using *Sediment Contaminant Bioavailability Assessment* (SCBA)



2. Anticipated Approach Using *Sediment Contaminant Bioavailability Assessment* (SCBA)



Four case studies are on-going to answer the question:

"How well does the SPME/SFE chemistry screen predict toxicity to amphipods?"

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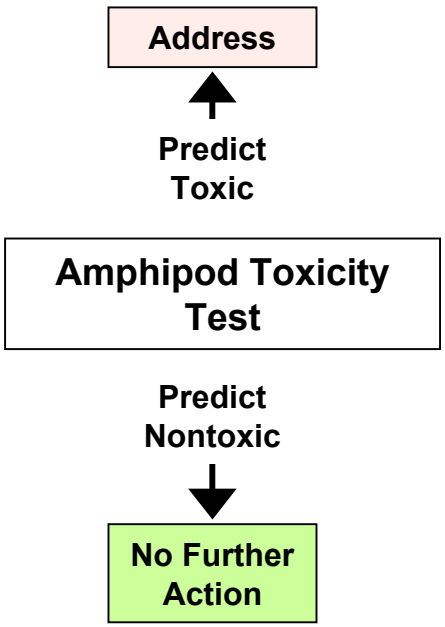
3. Anticipated Approach Using *Sediment Contaminant Bioavailability Assessment* (SCBA)



Additional studies will be required to answer:

"How well does the amphipod toxicity testing predict toxicity to other aquatic life?"

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Soil/Sediment Bioavailability Program

Interaction with regulatory agencies is key

- **Conduct technical workshops to key State Regulatory Agencies and EPA**
  - ✓ **New York DEC and DOH**
  - ✓ **New Jersey DEP**
  - ✓ **California EPA**
- **Developed Five-Year to Support Integration of Bioavailability Concepts into Federal and State Regulatory Guidance**

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Sediment Bioavailability Program

Major Program Tasks

- **Task 1 - Conduct Case Studies**
- **Task 2 - ASTM/EPA Approval of Analytical Methods**
- **Task 3 - Technology Transfer**
  - **Conferences**
  - **Peer-Review Publications**
- **Task 4 – Support Regulatory Guidance Development by EPA and ITRC**
- **Task 5 - Communication and Coordination**

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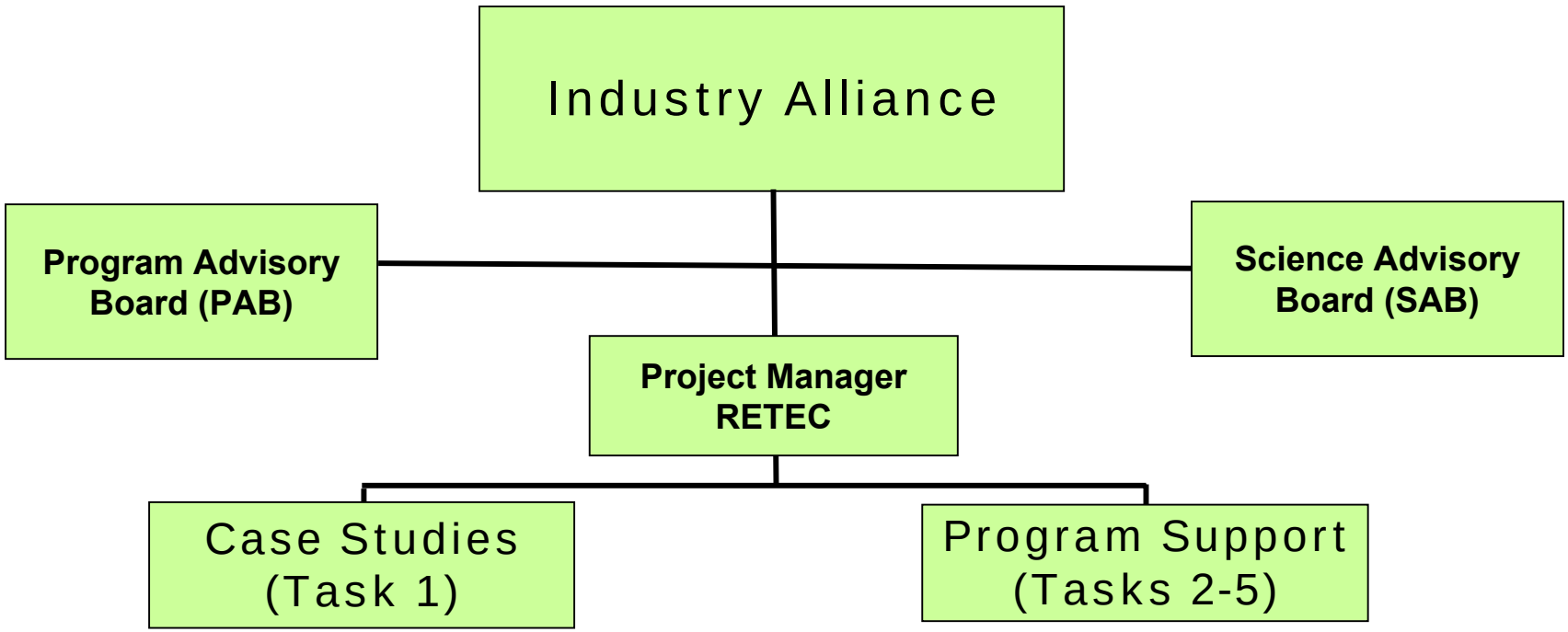
Proposed Alliance

Sediment Contaminant Bioavailability Program



- ✓ Utility Industry
- ✓ Aluminum Industry
- ✓ Steel Industry?
- ✓ Others …..?

2. Analytical Methods
3. Technology Transfer
4. Regulatory Guidance Support
5. Alliance Communication & Coordination

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Sediment Contaminant Bioavailability Alliance

Current Members

ALCOA

Niagara Mohawk
A National Grid Company

Northeast GAS ASSOCIATION

US Army Corps of Engineers

Interested Parties

USS

DUPONT

DOW

conEdison, inc.

bp

FPL

SOUTHERN CALIFORNIA EDISON
An EDISON INTERNATIONAL Company

ExxonMobil

AGL Resources

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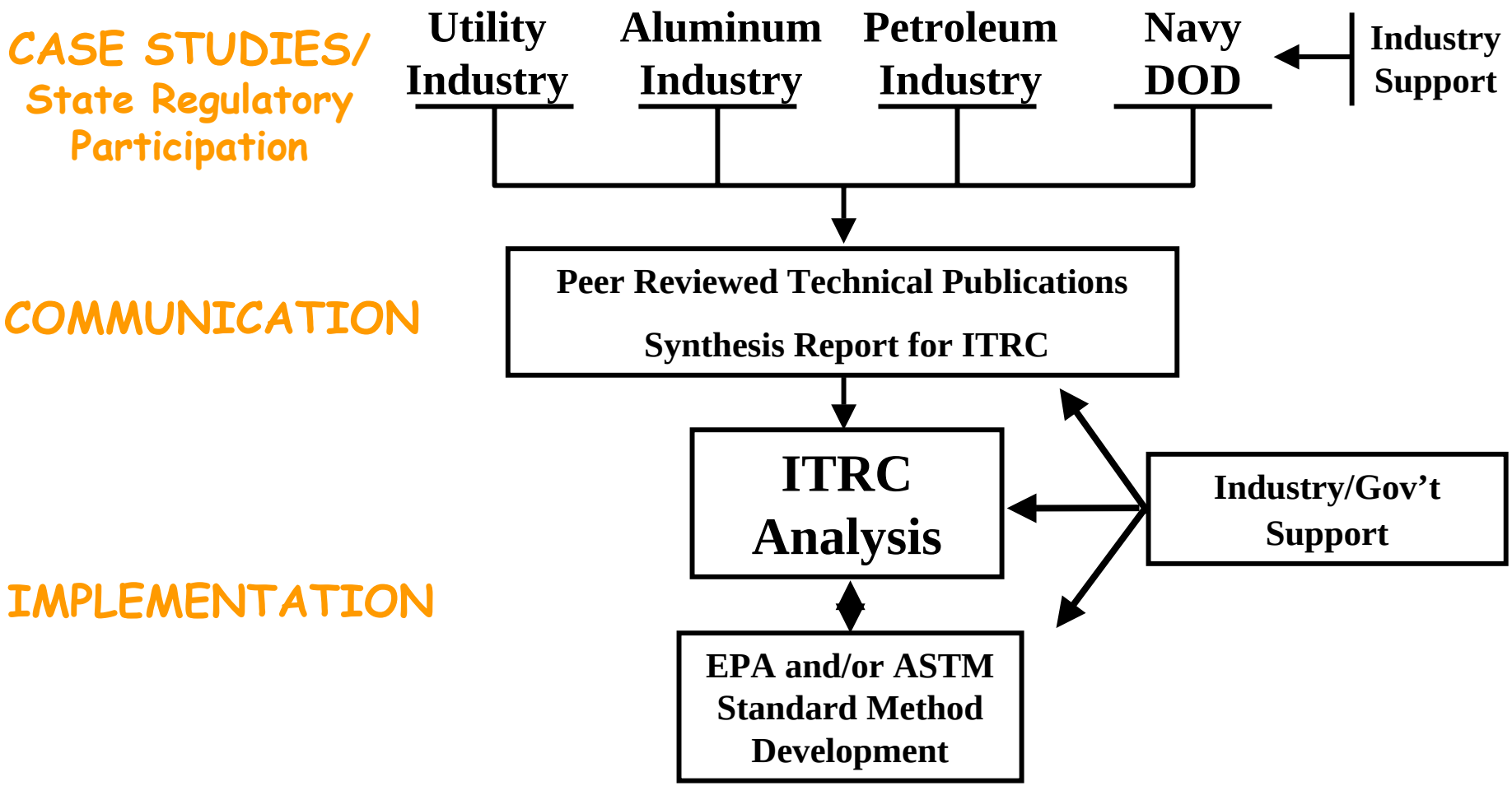
Multi-Industry Approach to Move Forward



Presentation Summary

- **Simple screening tools are needed which are appropriate for small “everyday” projects**
- **Interaction with state regulatory agencies is required to define “risk endpoints” requiring protection**
- **Case studies are necessary for gaining acceptance and to evaluate the effect of bioavailability data on sediment management**

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