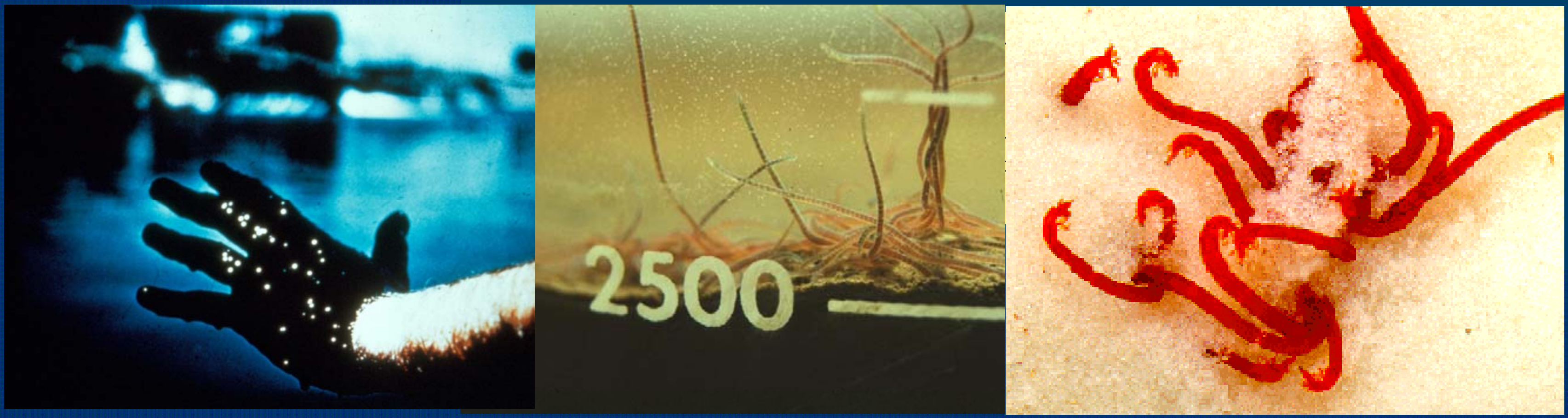
United States Environmental Protection Agency

Considerations for Predicting the Effects of Petroleum in Sediments

David R. Mount



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Types of Toxicity from Petroleum

- Conventional wisdom is that the toxicity of petroleum is attributable to the aromatic compounds, primarily polycyclic aromatic hydrocarbons (PAHs)
- Recent evidence that toxicity to some benthic organisms might also occur through another mechanism related to the presence of a non-aqueous phase, regardless of its composition

Three Key Issues for Assessing PAH Potency in Sediment

- Sediment organic carbon
  - Commonly ranging from 0.5% to 15% (30-fold)
- Bioavailability (coal, soot, tire rubber)
  - Can cause 100-fold difference
- Alkylation of PAH mixture
  - Easily a 10-fold difference
- In aggregate, the potential for a 30,000x range in threshold! (dwt, PP only)

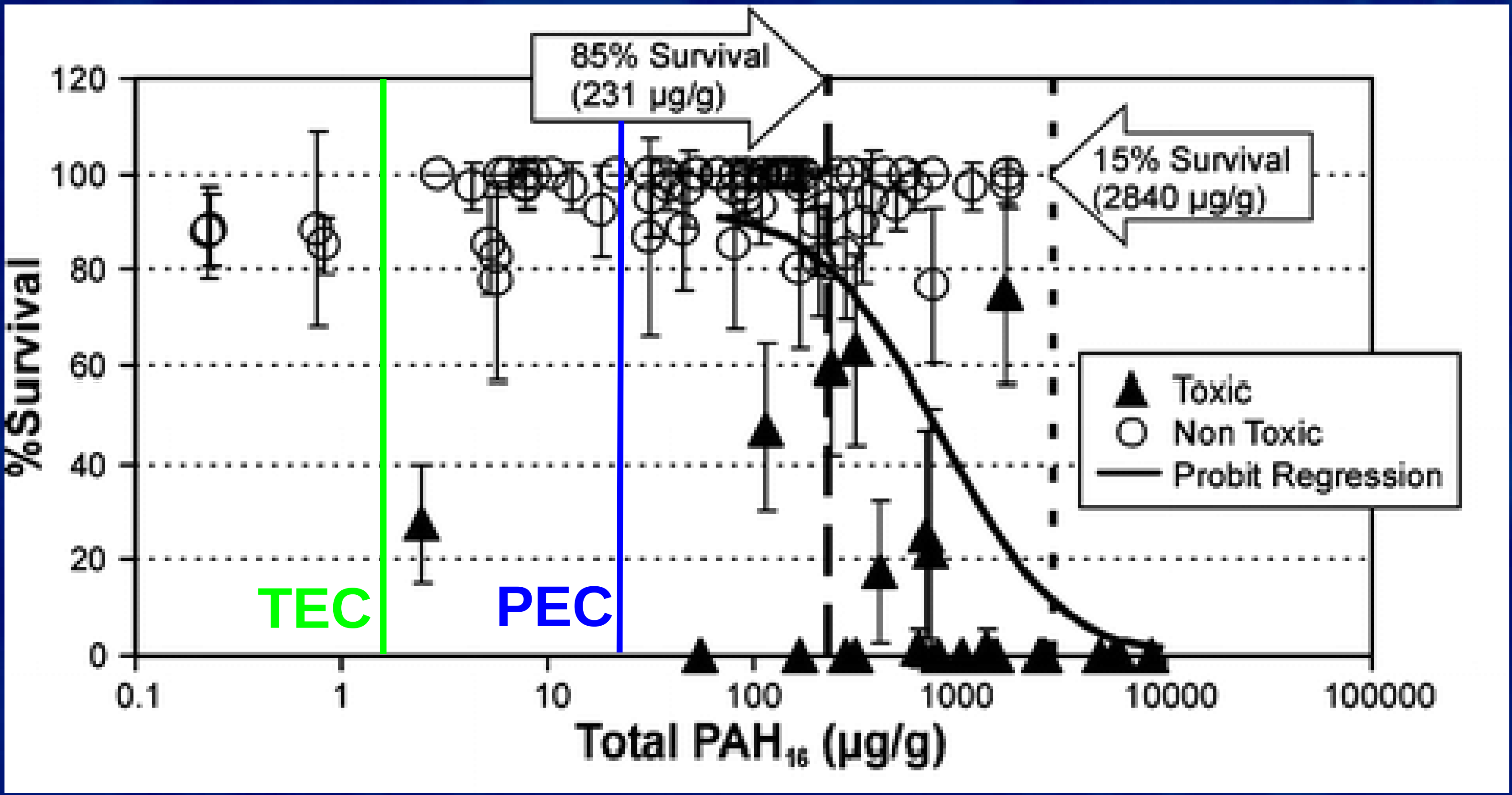
Types of Sediment Guidelines

- Empirical
  - ERL/ERM, TEL/PEL, TEC/PEC, AET, LRM
  - Based on databases of sediment chemistry and effect (toxicity) from a variety of sources
  - Expressions of the frequency of toxicity occurrence/non-occurrence as a function of sediment contamination
- Mechanistic
  - Equilibrium partitioning, EPA ESB
  - Predict sediment toxicity based on laboratory toxicity test data and contaminant partitioning between solid phase and interstitial water

Empirical Guidelines

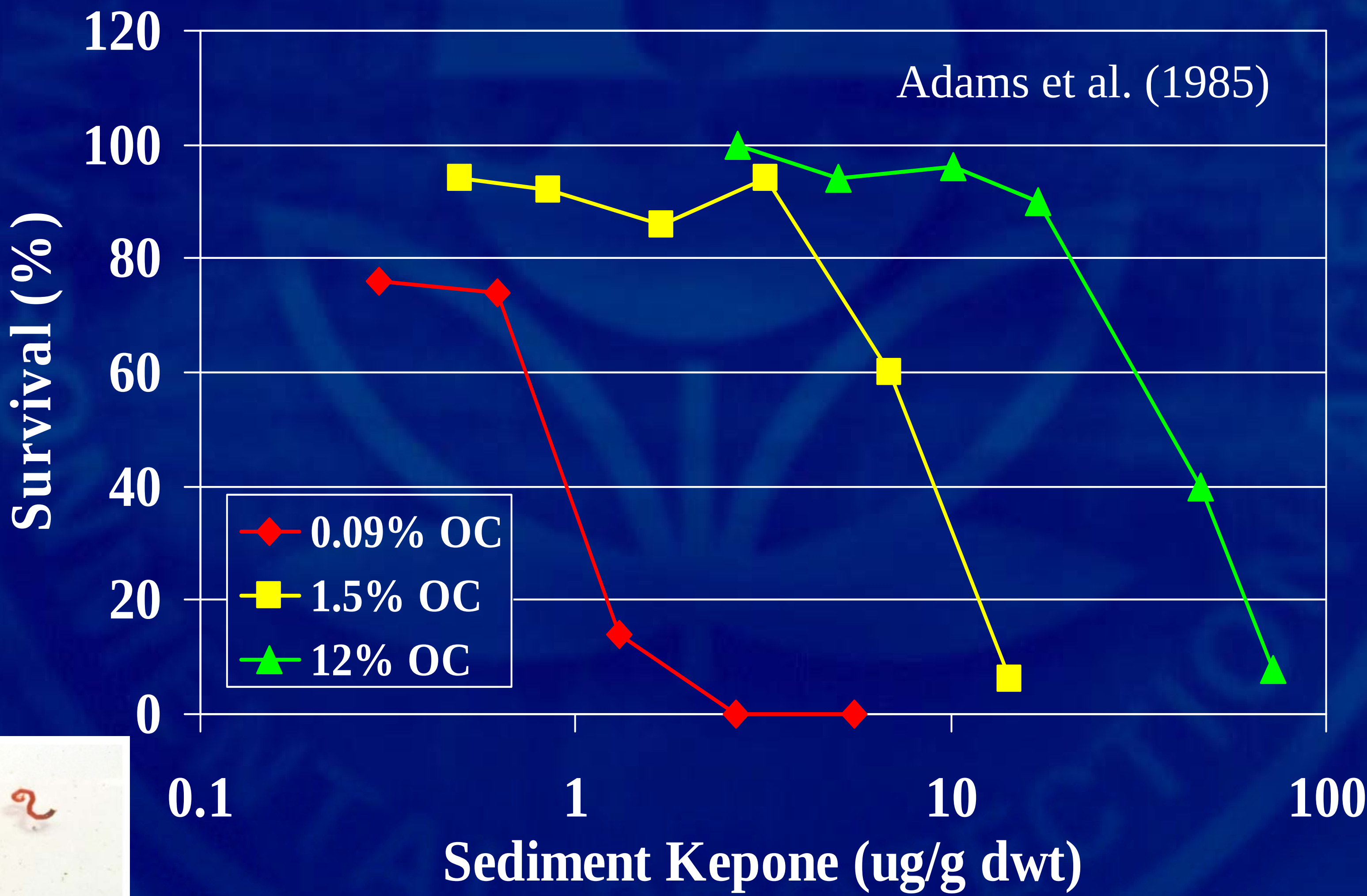
- Most are based on dry weight normalized concentrations in sediment
- Shown to be useful screening tools
- Don’t explicitly account for PAH mixture composition or bioavailability
- Values reflect an “average” of these factors across the data on which they are based

Dwt-Normalized Priority Pollutant PAH v Toxicity to *Hyalella*



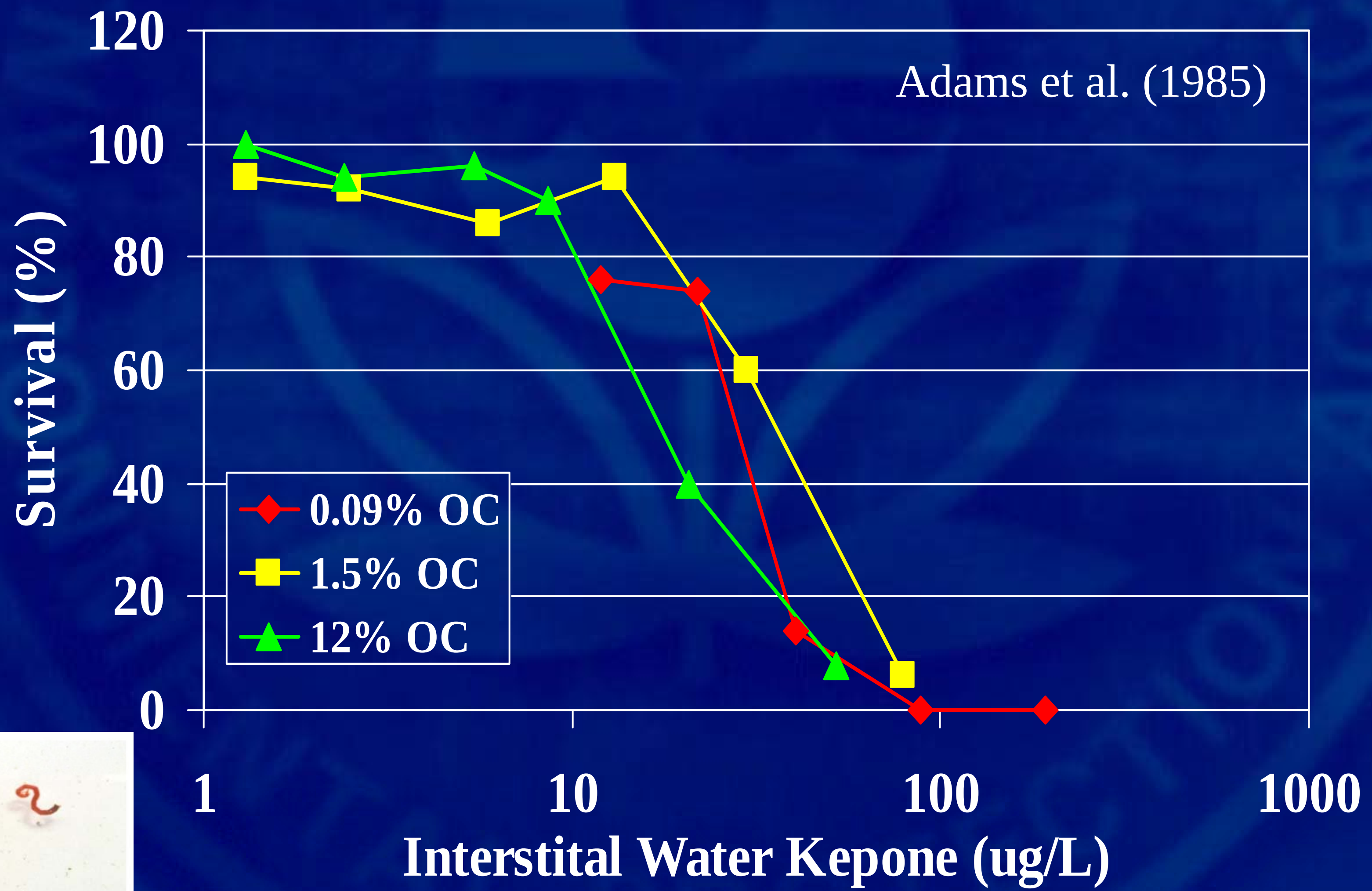
Data from Hawthorne et al 2007

Response Midge Larvae to Kepone in Sediment
Dry Weight Normalization



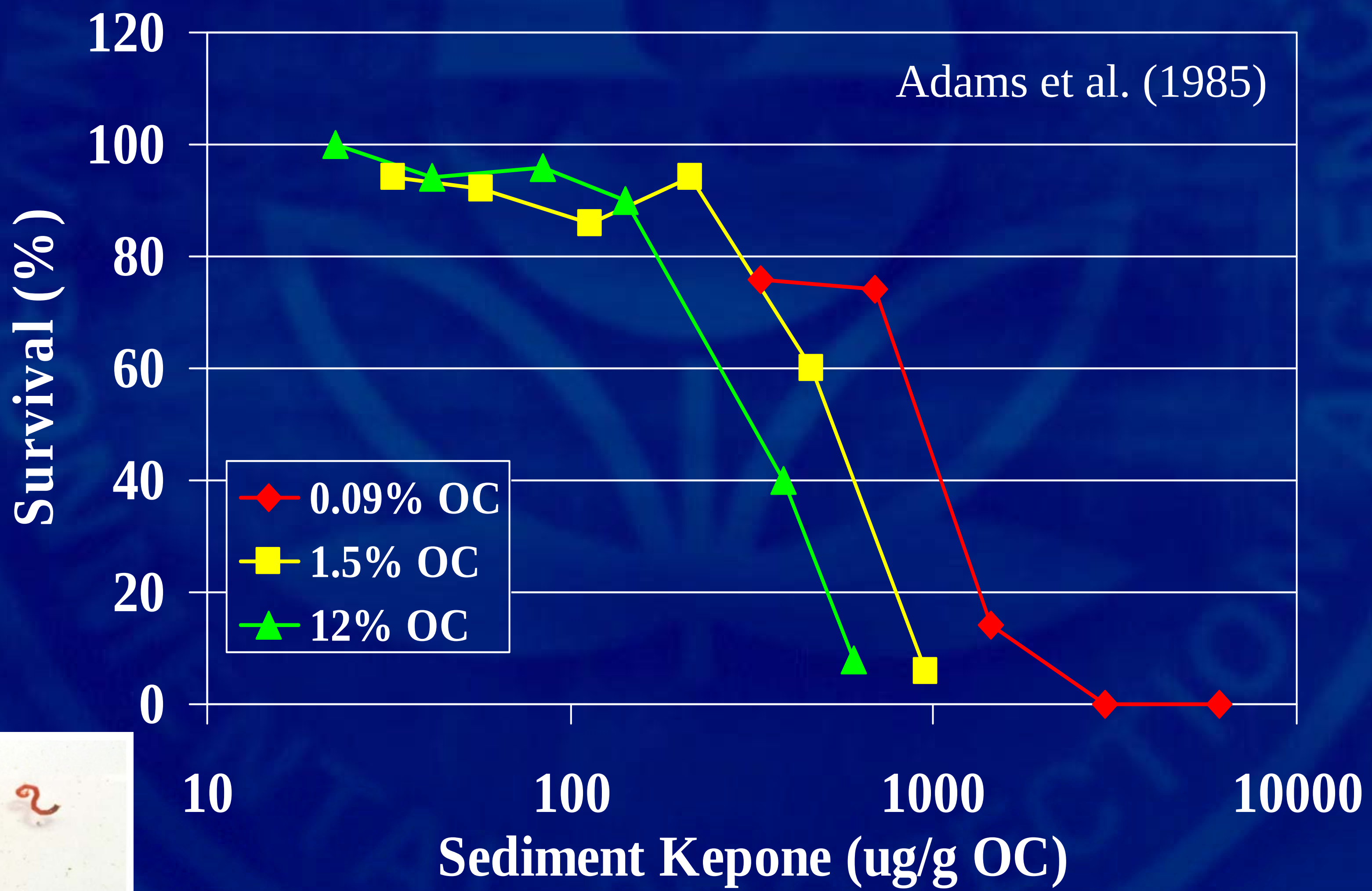
Response Midge Larvae to Kepone in Sediment

Interstitial Water Normalization



Response Midge Larvae to Kepone in Sediment

Organic Carbon Normalization

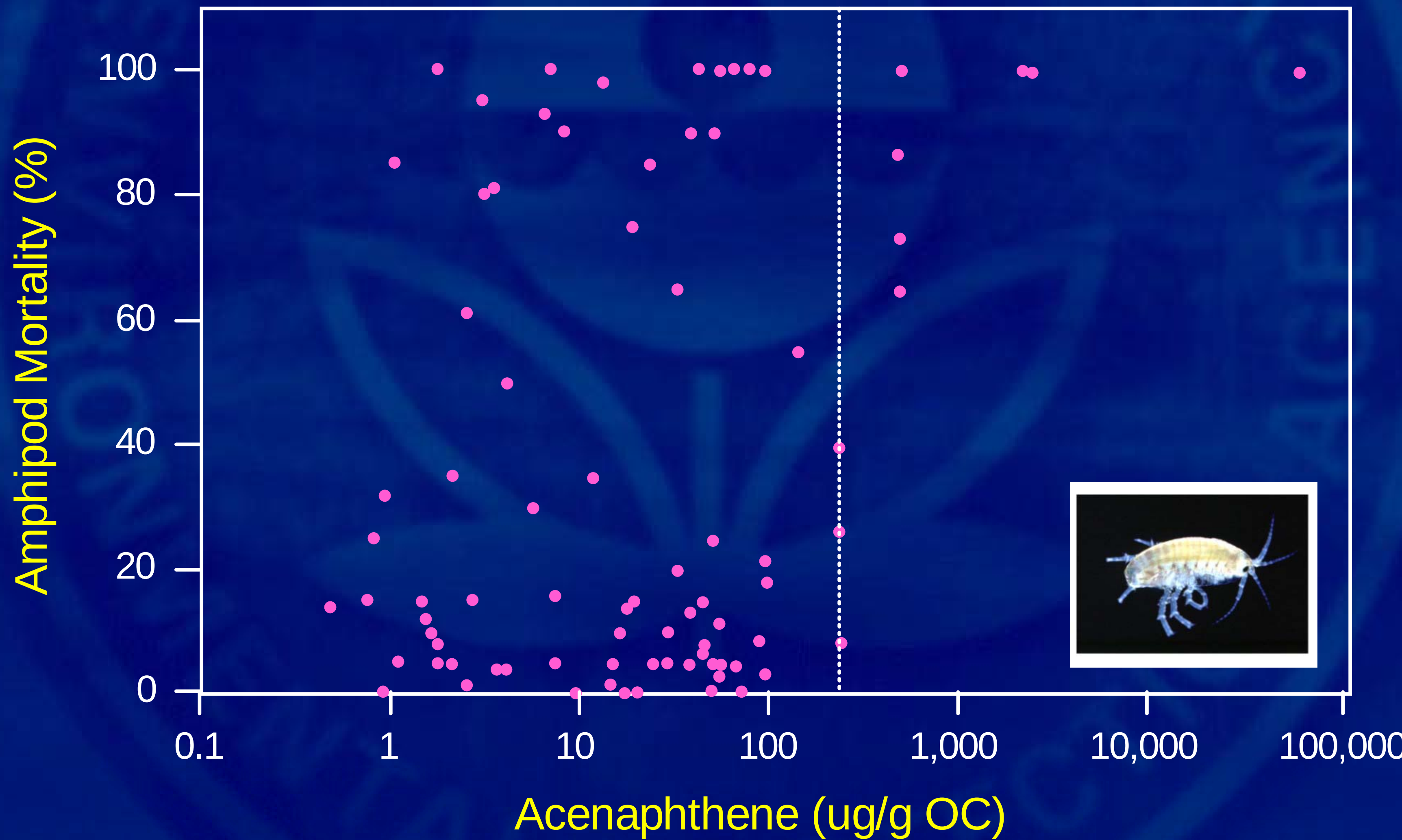


Establishing Biological Effect Concentrations in Sediment

- Basic Partitioning: $C_{soc} = C_{iw} * K_{OC}$
- Biological Effect: $C_{soc} = C_{effect} * K_{OC}$
- Sediment “Criteria”: $C_{soc} = C_{AWQC} * K_{OC}$
- Equilibrium Partitioning Sediment Benchmarks (ESB)

Mortality of Amphipods in PAH-Contaminated Sediments

Organic Carbon-Normalized Acenaphthene Concentration



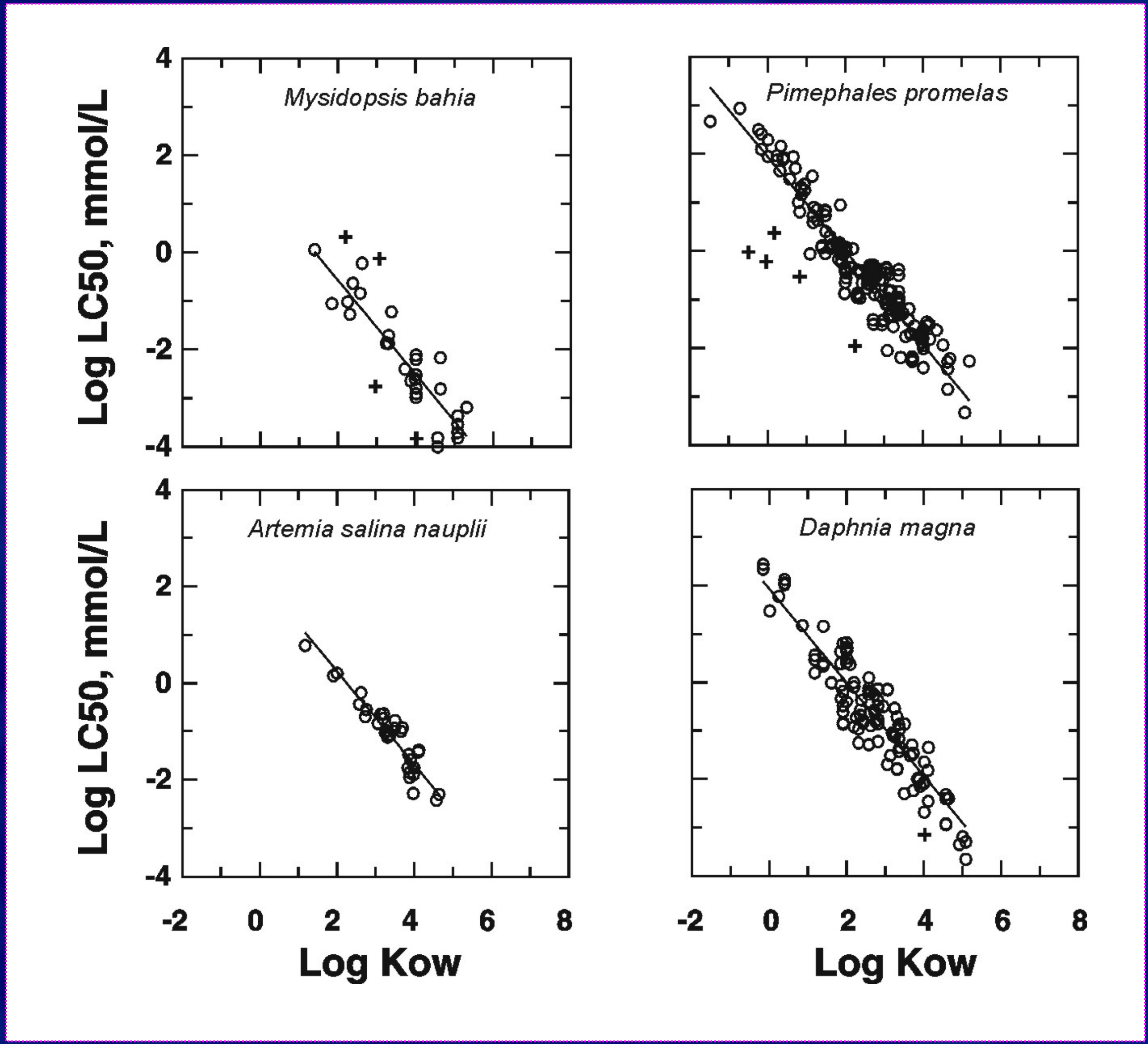
Swartz (1999)

Issues for Developing PAH ESB

- There are hundreds of PAH structures
- PAHs always occur as mixtures
- Needs for ESB development
  - Way to predict toxicity of all PAHs
  - How to integrate toxicity of mixtures
- PAH ESB available at: www.epa.gov/nheerl/publications

Narcosis Toxicity Related to Kow

DiToro et al. 2000



Toxicity of PAH Mixtures

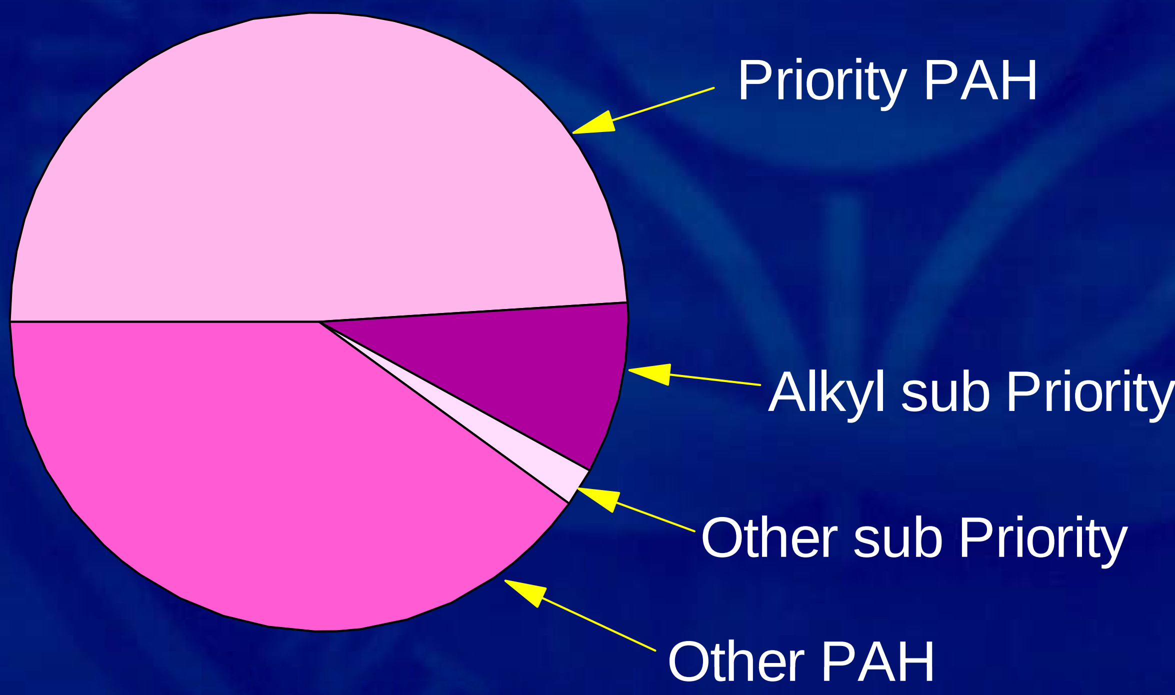
- Chemicals with a common mode of action generally show additive toxicity
- Contribution of each chemical to the mixture is represented by its “Toxic Units”
- Toxic units are the ratio of the concentration to the concentration of that single chemical that would cause effects

PAH Mixture Methodology

- Using narcosis theory and Kow/Koc relationships, calculate a sediment guideline for a single PAH
- For each PAH, divide the OC normalized sediment concentration by the PAH-specific guideline value (“guideline units”)
- Sum guideline units across all PAHs; if sum exceeds 1, then guideline is exceeded

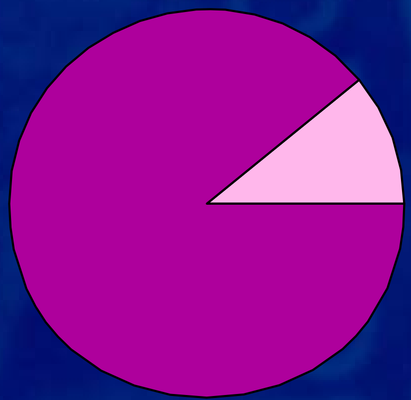
Relative Composition of PAH Sources

Coke Plant Sediments

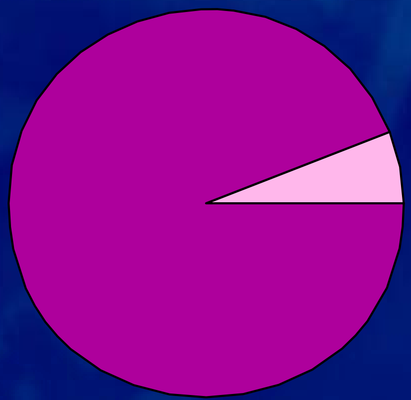


Burkhard et al. 1994

North Slope Crude

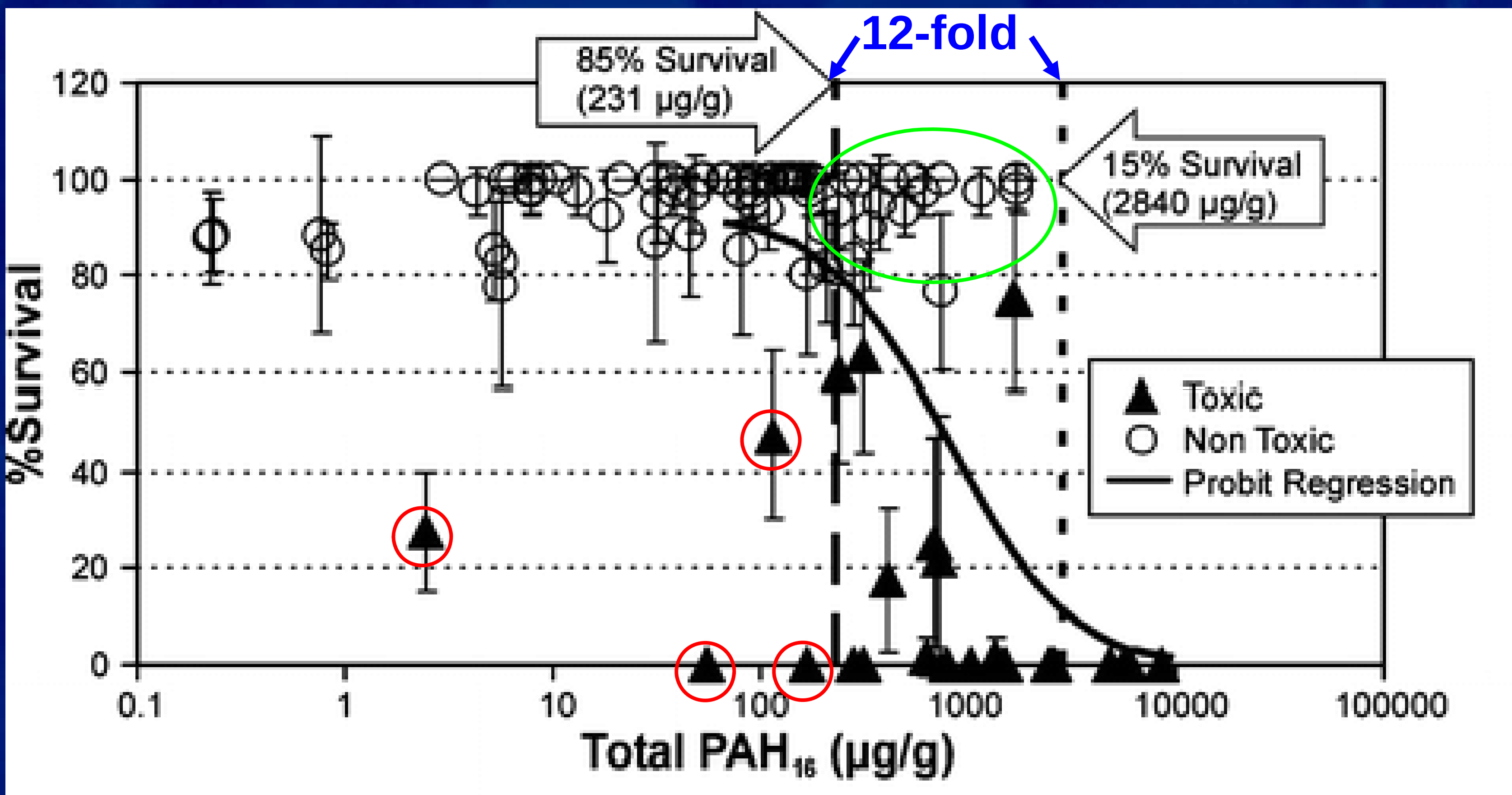


Weathered NS Crude



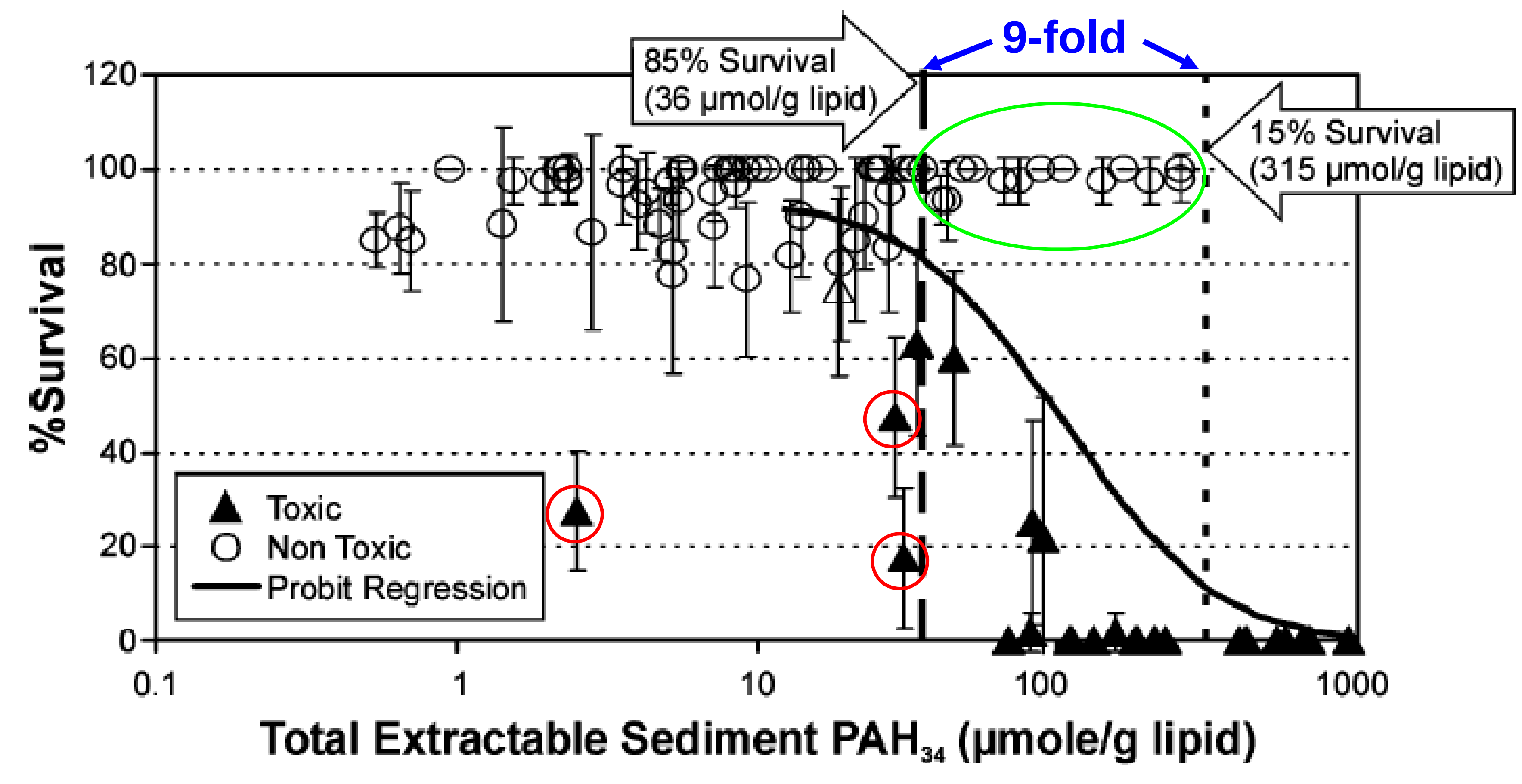
Stubblefield et al. 1995

Dwt-Normalized Priority Pollutant PAH v Toxicity to *Hyalella*



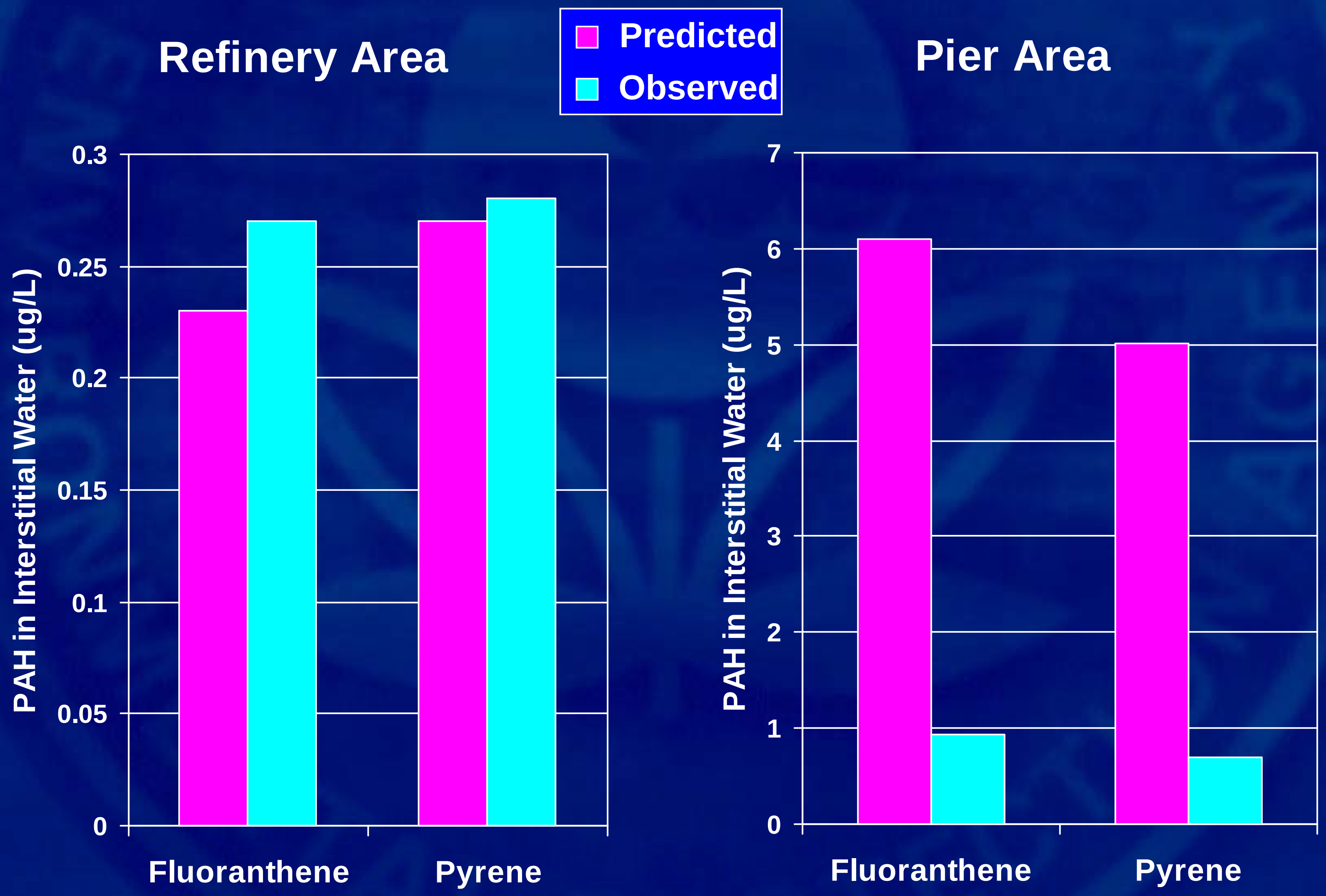
Data from Hawthorne et al 2007

OC-Normalized PAH34 v Toxicity to *Hyalella*



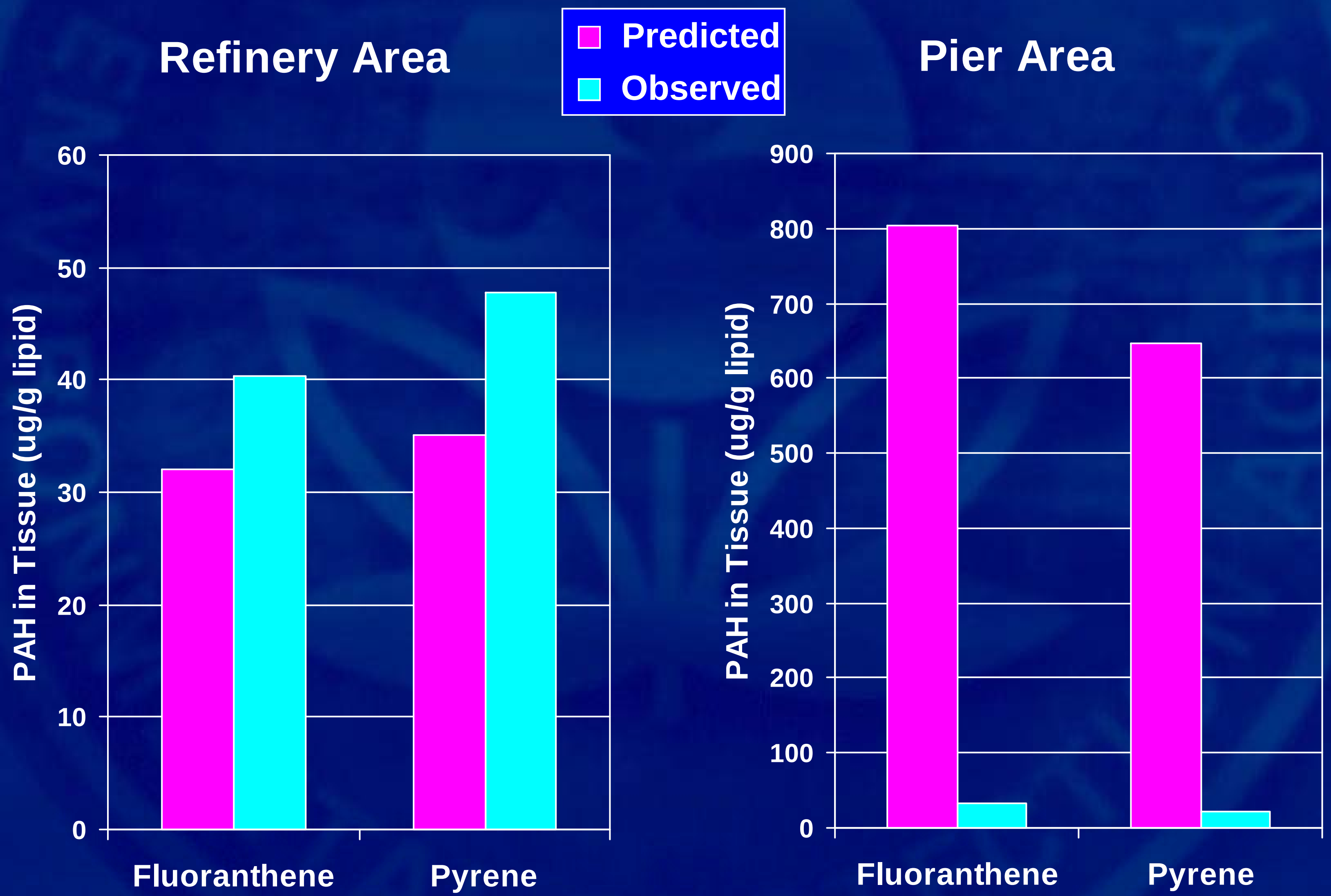
Data from Hawthorne et al 2007

PAH Partitioning Behavior



West et al. 2001

PAH Accumulation in Oligochaetes

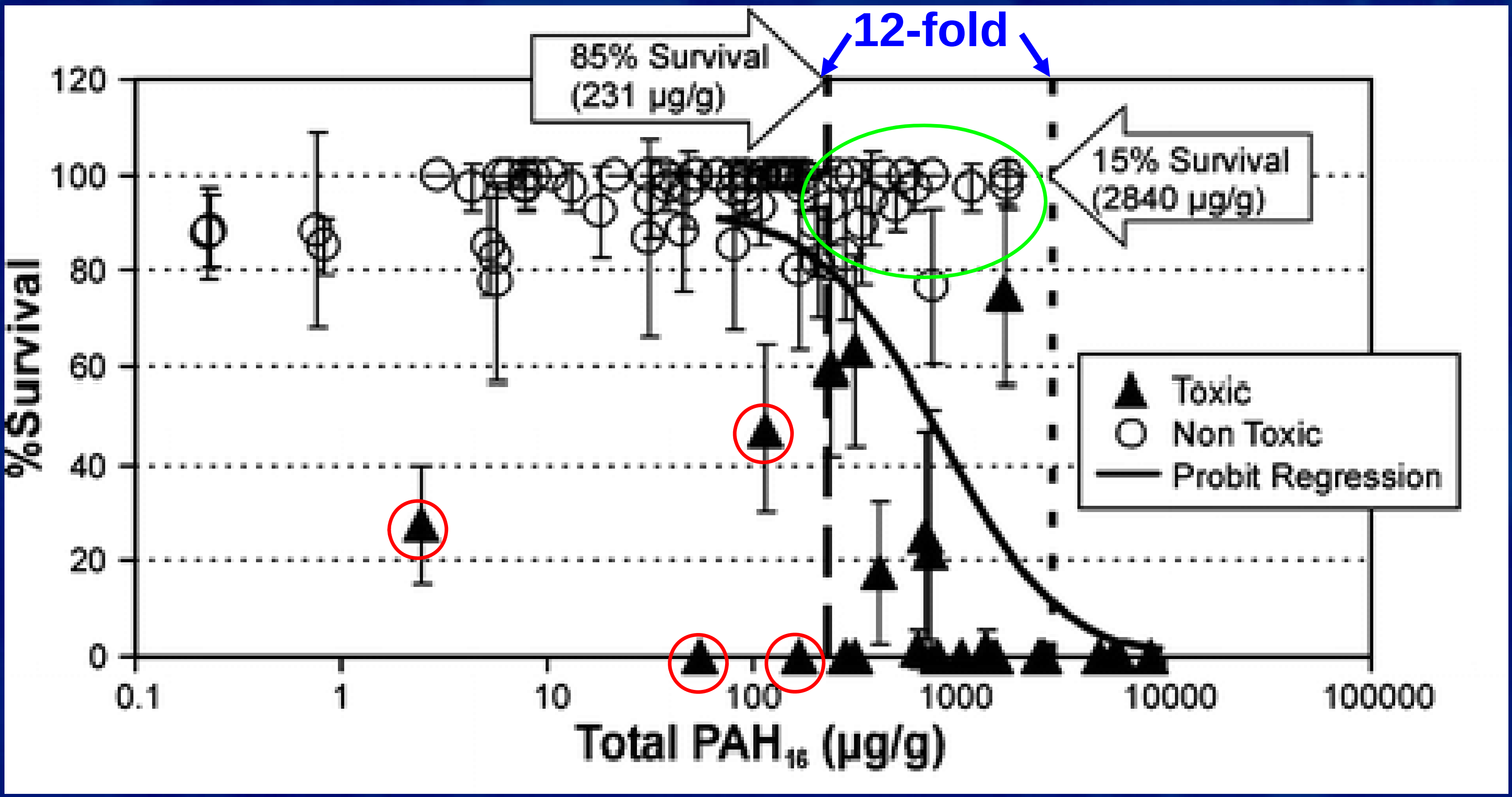


West et al. 2001

Incorporating Bioavailability into Sediment PAH Assessment

- “Black carbon”, such as soot, coal, pitch, tire rubber, can contain PAHs that are much less bioavailable than in ordinary organic carbon
- Lower bioavailability is reflected in lower PAHs in interstitial water and tissues
- Methods such as solid-phase micro extraction (SPME) can be used to quantify IW PAHs and correct for bioavailability

Dwt-Normalized Priority Pollutant PAH v Toxicity to *Hyalella*



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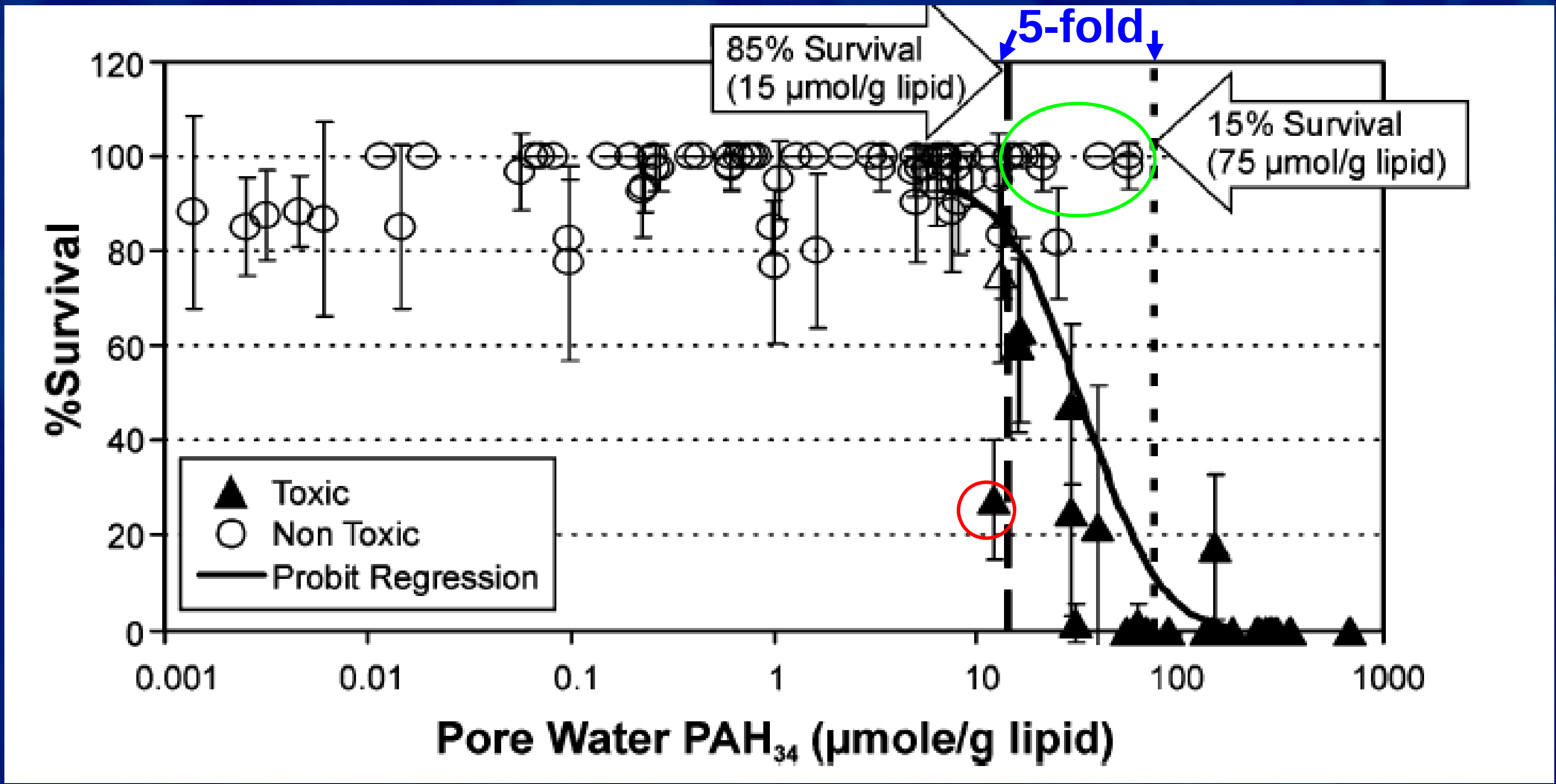
SPME-measured IW PAH v Toxicity to *Hyalella*



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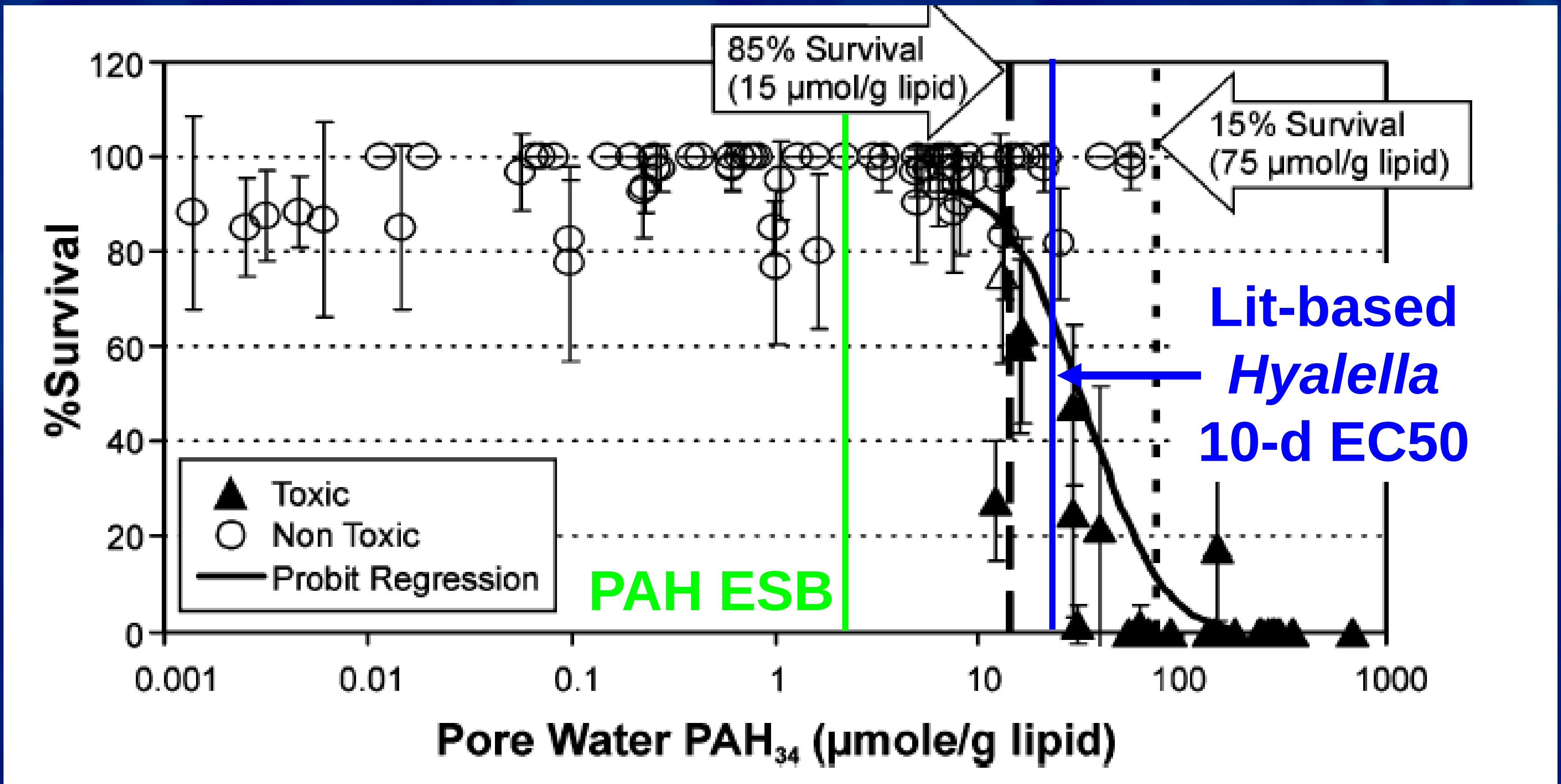
SPME-measured IW PAH v Toxicity to *Hyalella*

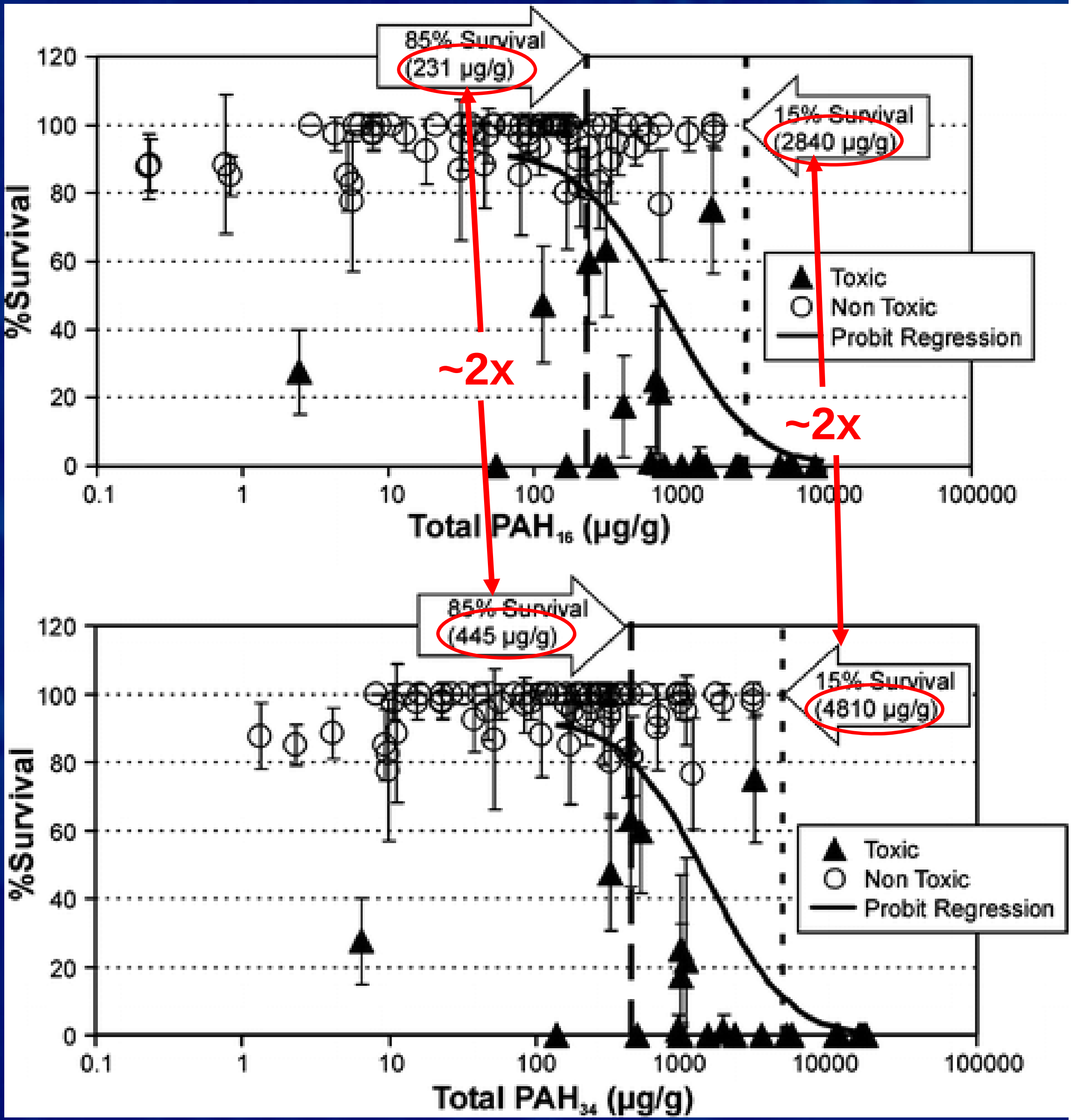


Data from Hawthorne et al 2007

Hawthorne (2007) data relatively low in alkylation

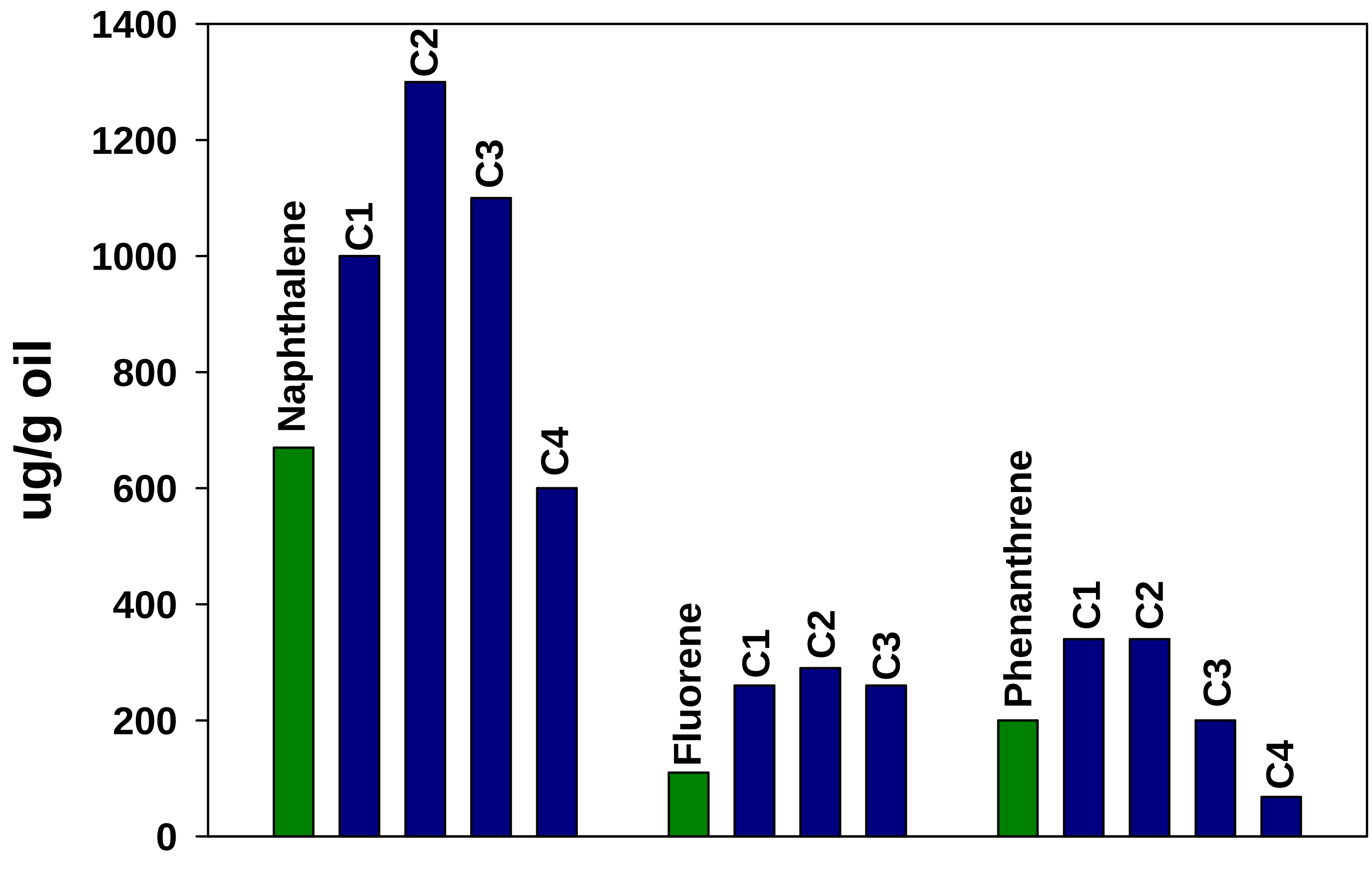
Median ratio of PAH_{16} to only 2.1

This is typical of coal tar, but not of petroleum



Data from Hawthorne et al 2007

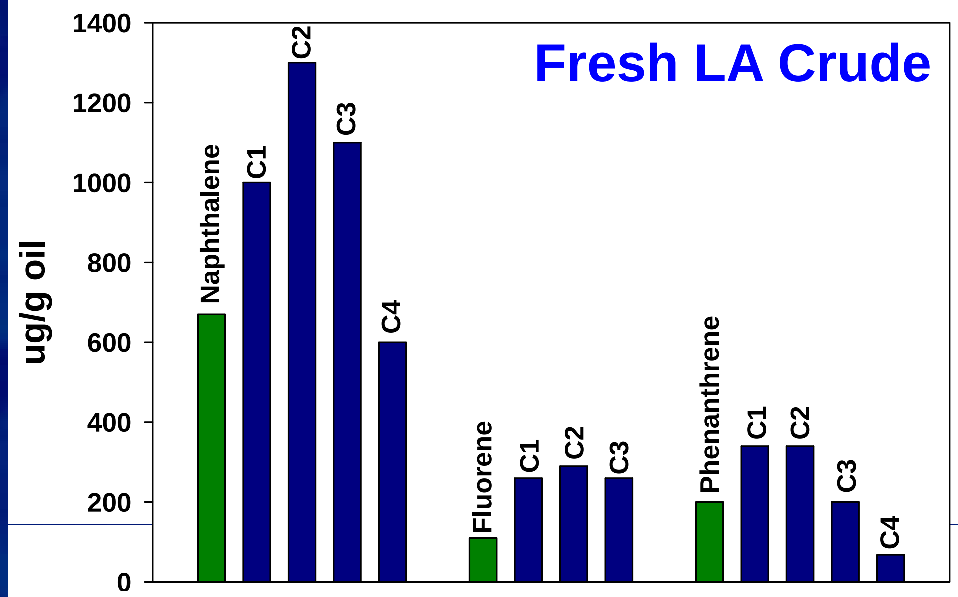
Alkylation Patterns in South Louisiana Crude

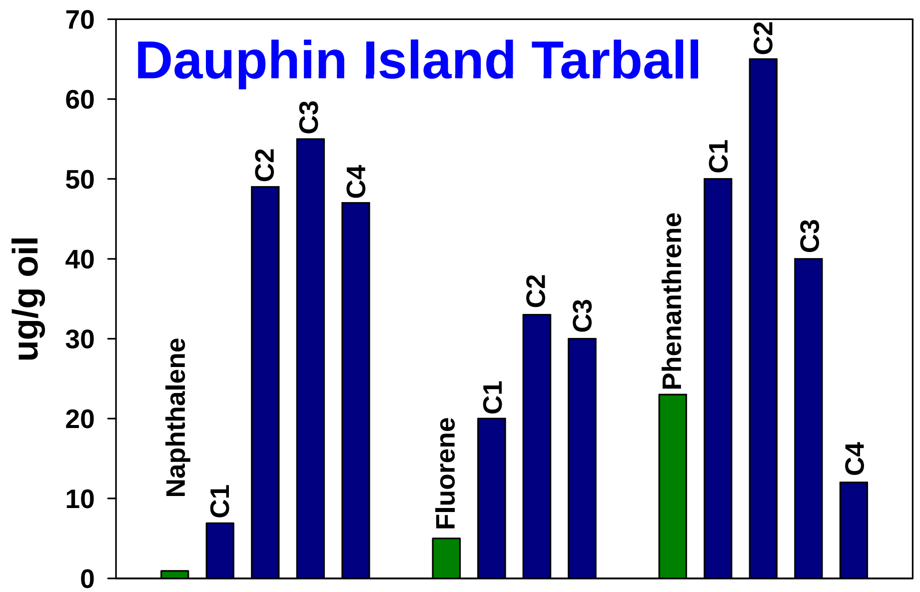


Alkylation high in both fresh and weathered oil

However, ratio of PAH34 to PAH 16 increases with weathering

Assessment based on only parent PAHs will become increasingly inaccurate with weathering





Effect of Alkylation on Toxicity Estimation

- Calculated under-estimation of toxicity when assessing PAH_{16} v PAH_{34}

Oil Source	n-fold Under-estimation
Exxon-Valdez Crude	7.7
Weathered E-V Crude	22.1
Fresh South LA Crude	5.4
Dauphin Island Tarball	7.2

PAH Toxicity Mechanisms Other Than Narcosis

- PAH ESB assumes narcosis is the mode of action for PAHs; generally accepted as true for benthic invertebrates
- Some responses to PAH exposure are not those typically associated with narcosis and may require additional assessment components
  - Chronic toxicity to early life stage fish
  - Photo-activated or photo-enhanced toxicity

Which Sediment Guideline is Best?

- There are no bad guidelines, only guidelines used badly
- The issue is applying guidelines in ways that
  - Are consistent with their derivation
  - Recognize the implicit assumptions and uncertainties
  - Address the realities of PAH bioavailability and toxicity
  - Are consistent with the management objectives
- Modified EqP approach with SPME IW PAH measurement is well suited to address PAH toxicity from the Deepwater Horizon event

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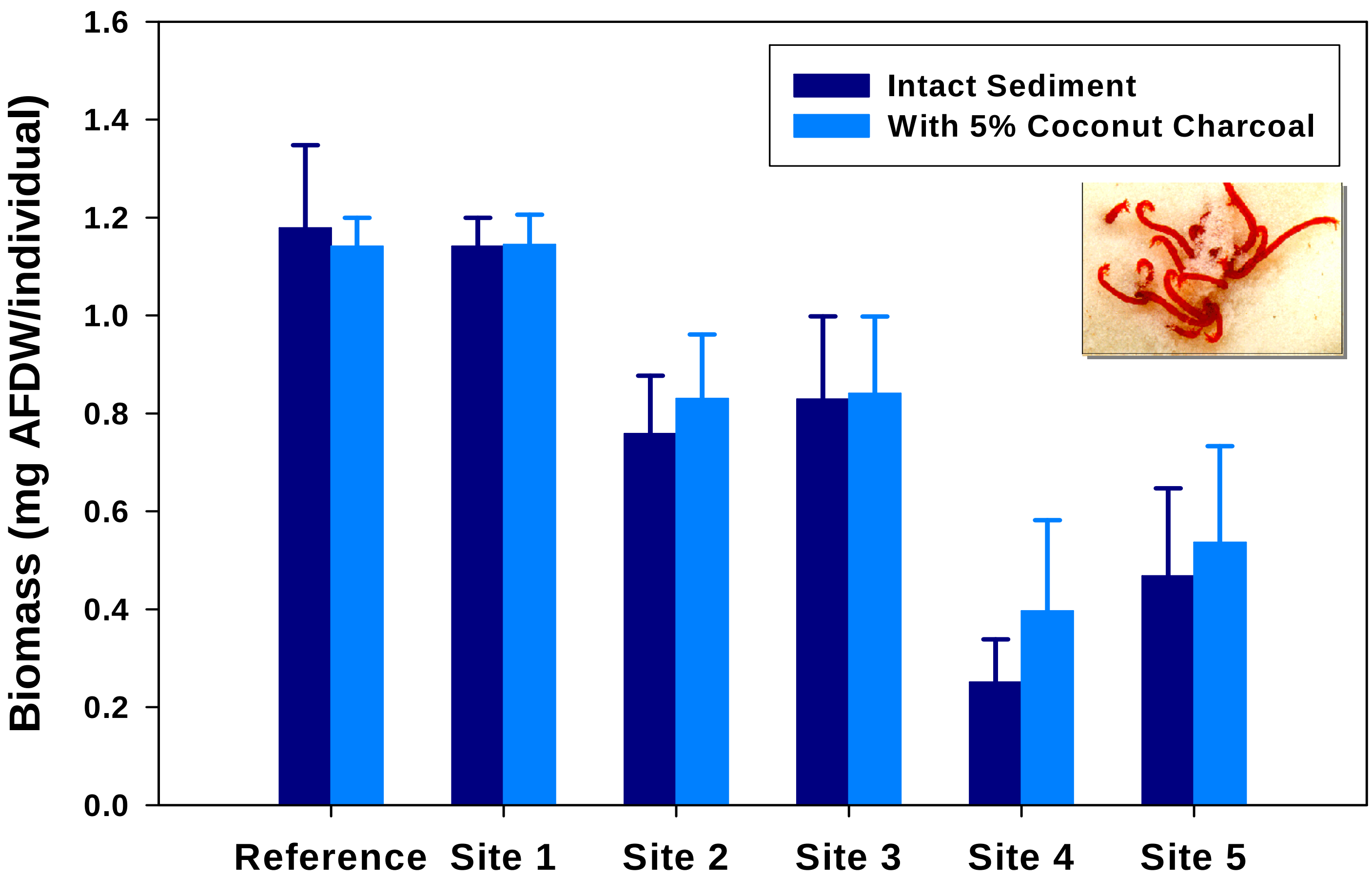
Can We Really Ignore Oil Components Other Than PAHs?

- By mass, PAHs are only a small fraction of total hydrocarbon mass in petroleum
- Alkanes, cycloparaffins and other components of non-aqueous phase liquids are typically thought to contribute little to toxicity
- Extensive experiments looking at water-accommodated fractions of oil and compound-specific toxicity support this presumption
- Recent evidence suggest it may not be true in sediments for some benthic invertebrates

Coconut Charcoal Did Not Reduce Toxicity of PAH-Contaminated Sediments



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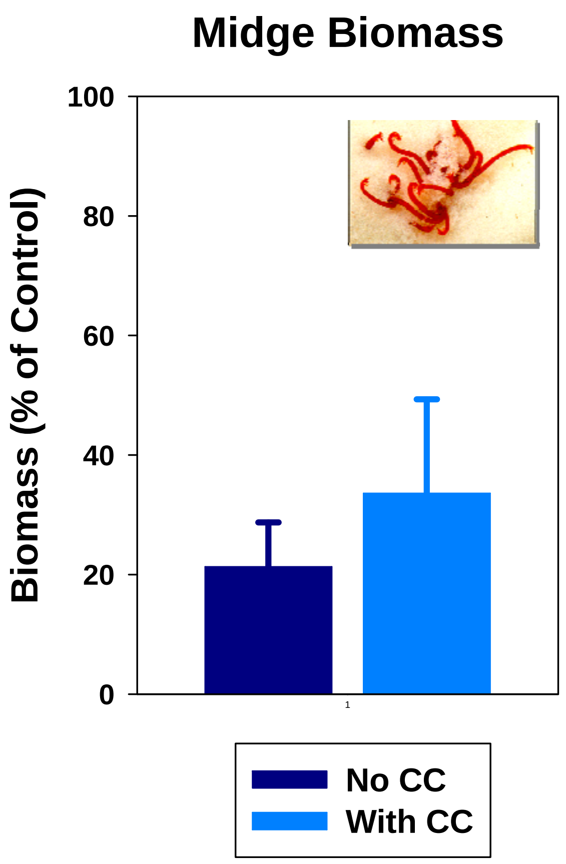
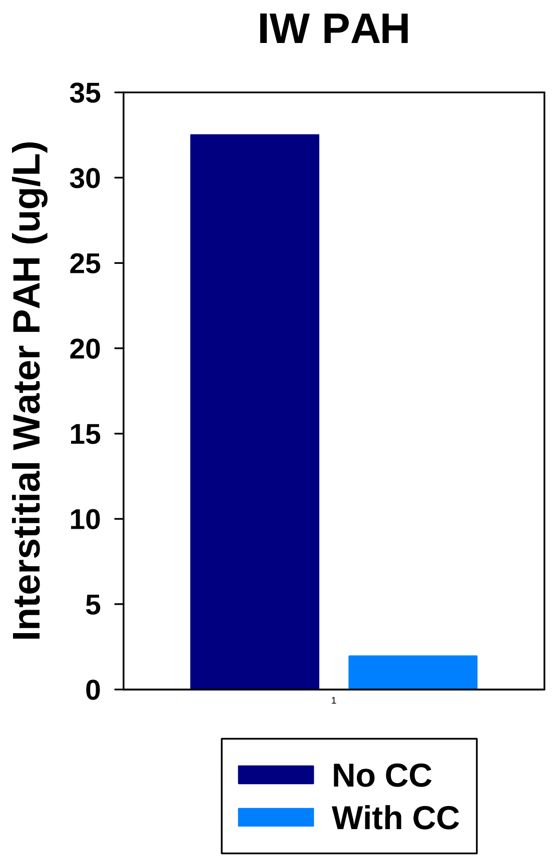
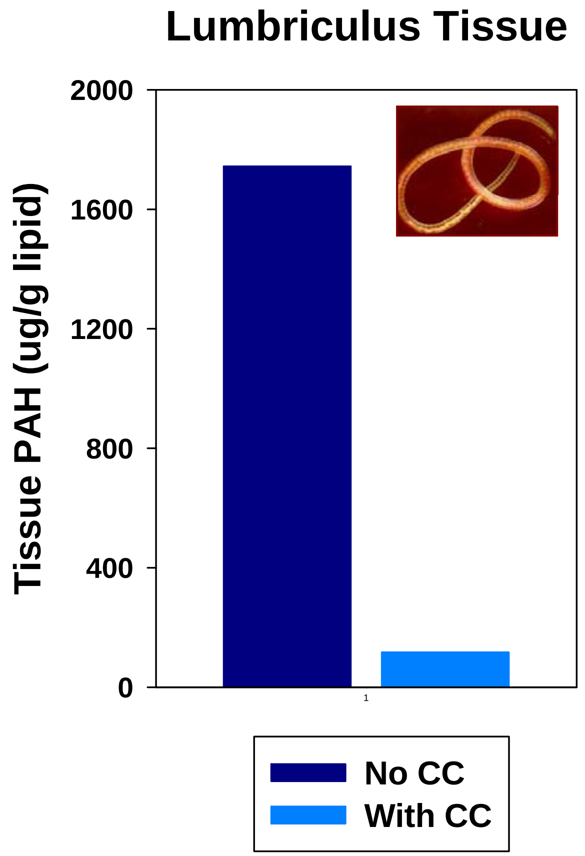
Charcoal Reduces PAH Bioavailability But Not Toxicity







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Mineral Oil as a Model Oil

- So-called “baby oil” without the scents
- Comprised mainly of alkanes in the C13 to C24 range
- Essentially no PAH content
- Considered non-toxic
- Water-accommodated fraction not toxic to test organisms
- Intended to represent the “oil” part of contamination without the PAH part

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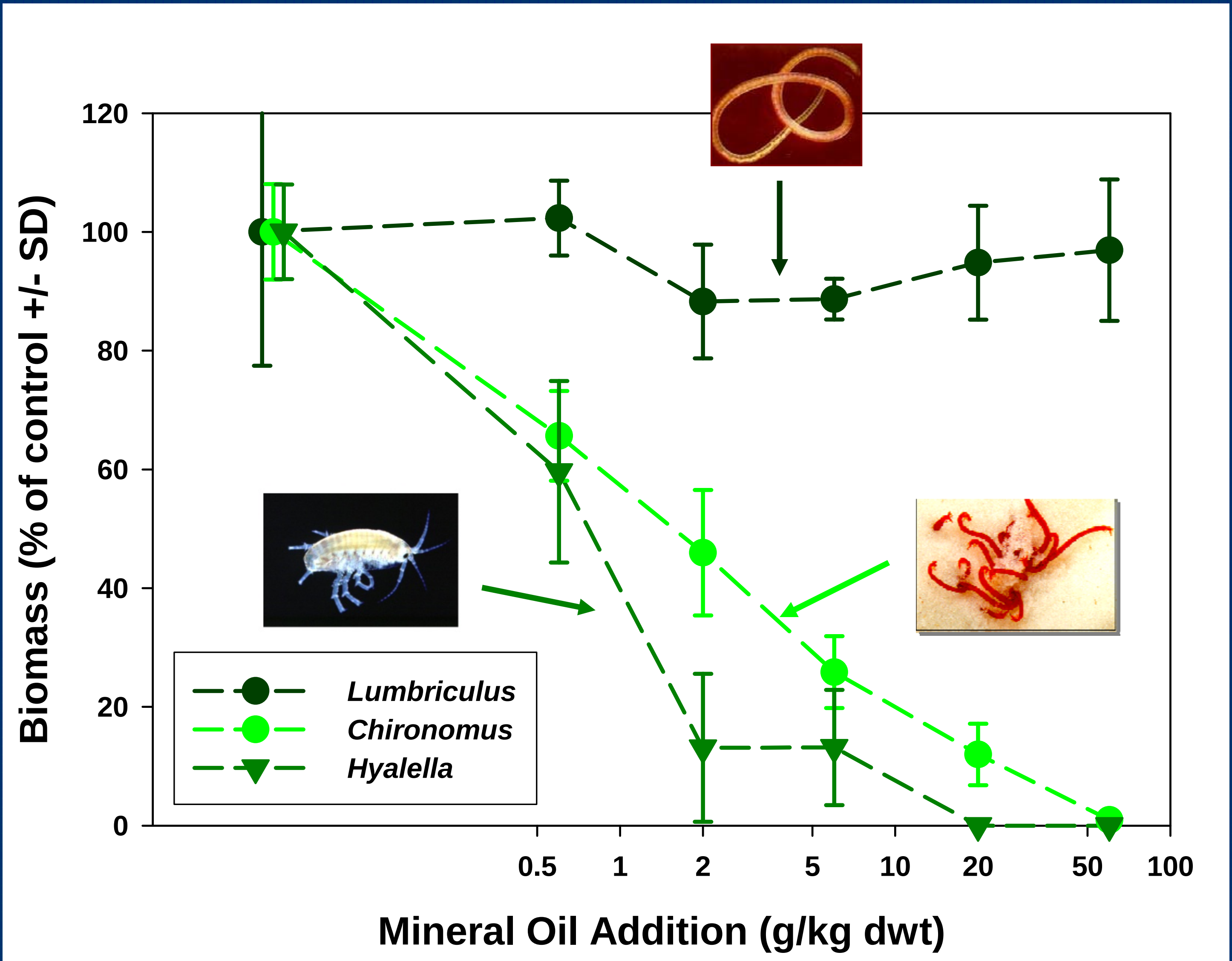
Mineral Oil Toxic to *Hyalella* and *Chironomus*



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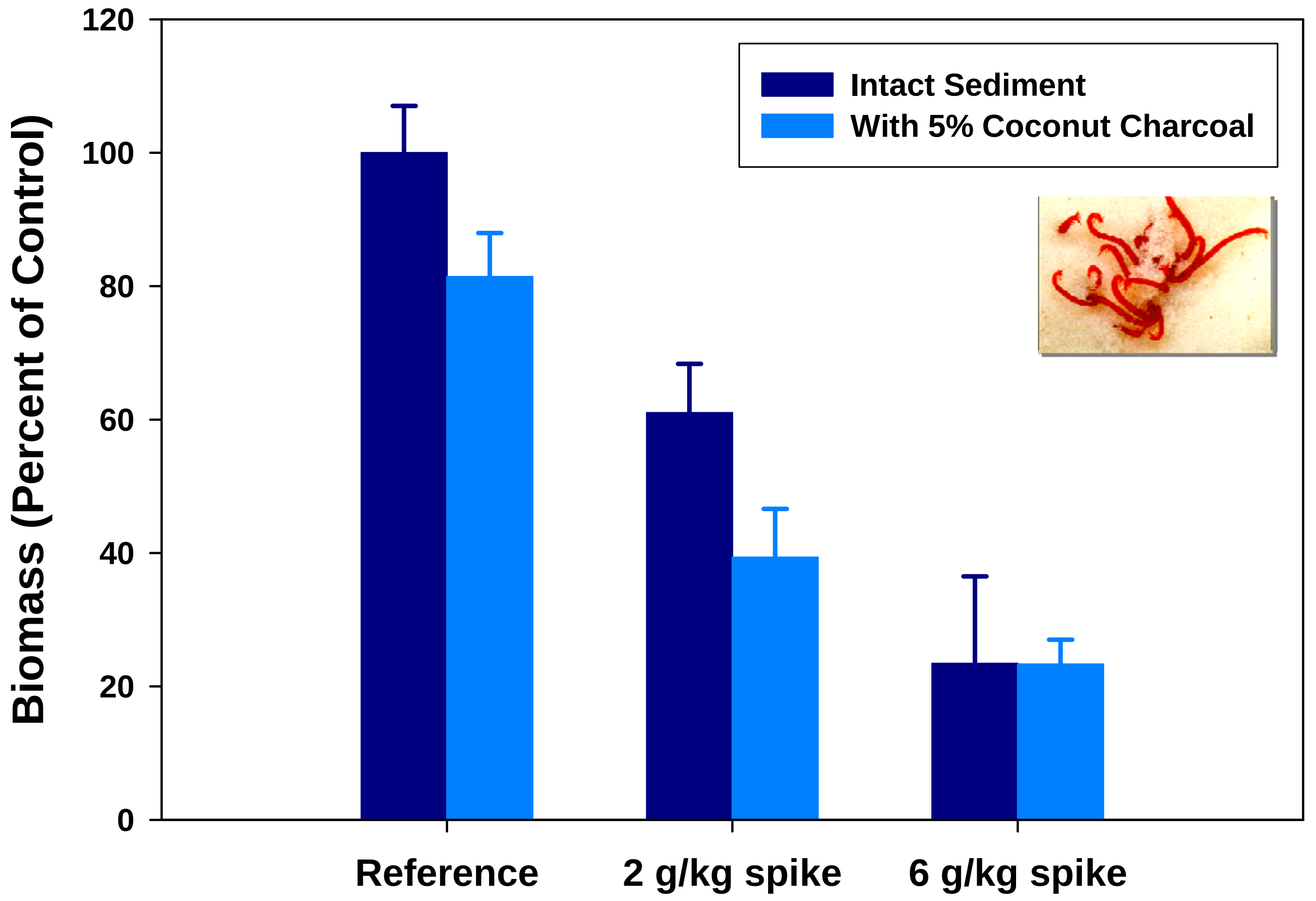
Charcoal Does Not Affect Toxicity of Mineral Oil



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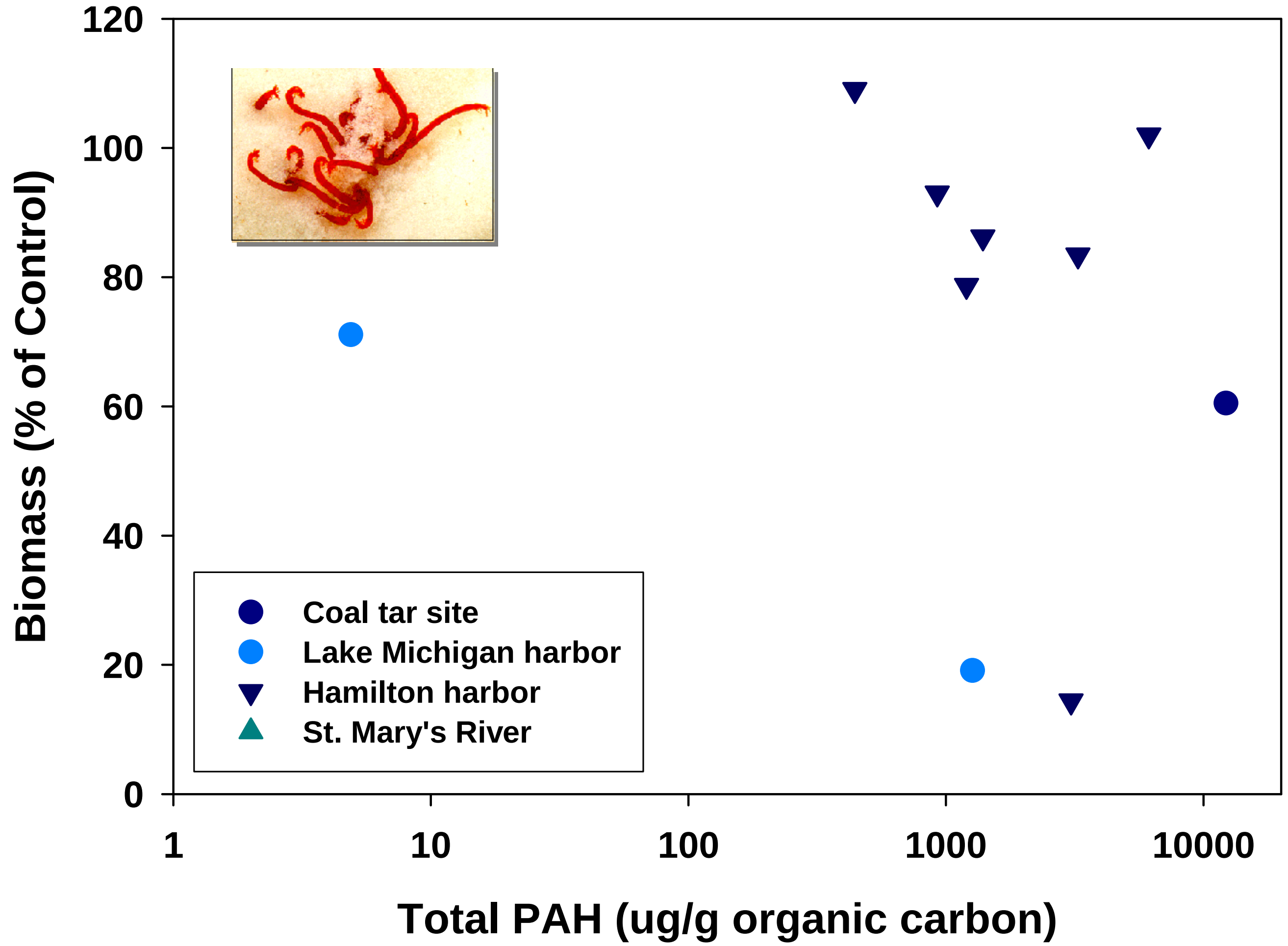
Toxicity of Field Sediments Not Well Correlated with PAH



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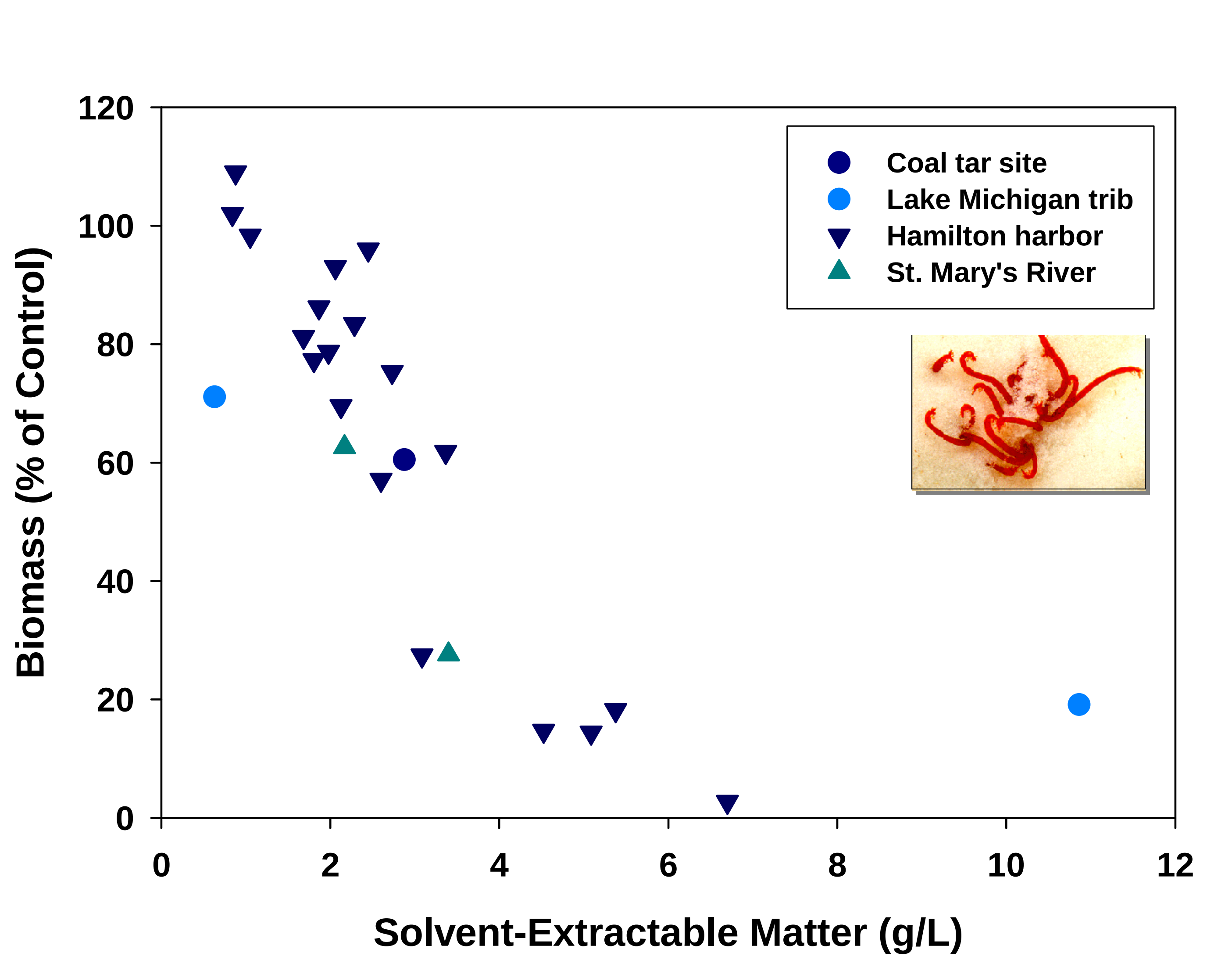
Solvent Extractable Matter Correlates Well with Toxicity



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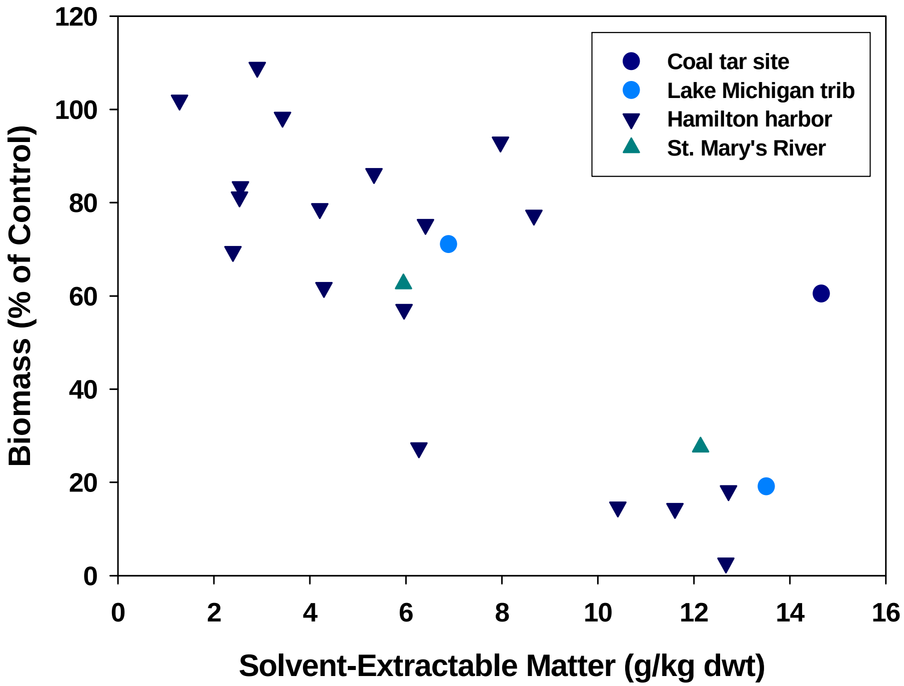
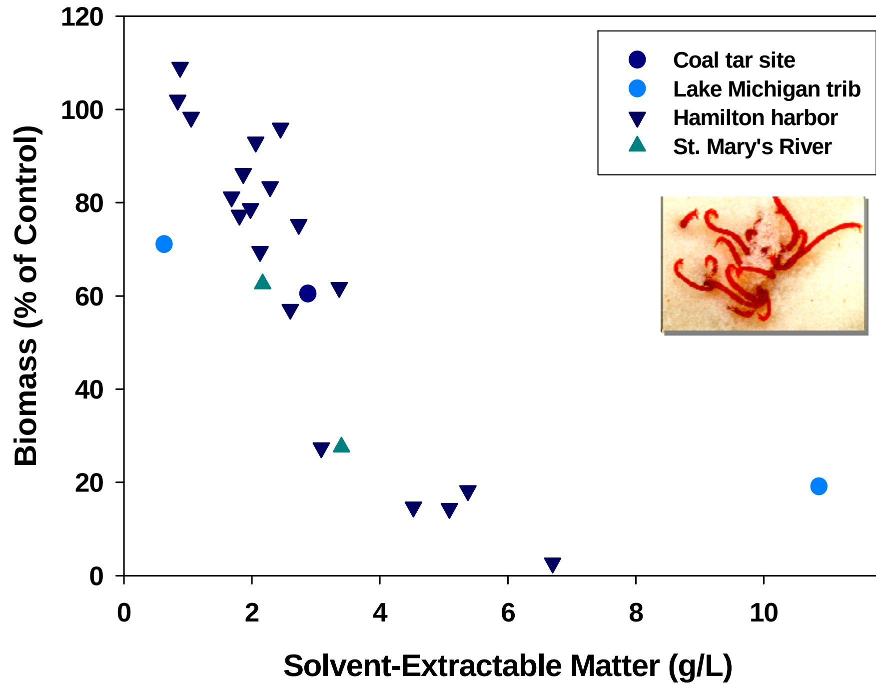
Toxicity Correlates Better With Volume Normalization

Normalized to Dry Weight



Normalized to Volume



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Why Volume Normalization?

- If mineral oil toxicity is from physical contact, it follows that the potency of exposure would be linked to the likelihood of encountering oil
- Two sediments, A and B, both with 1 g/kg dwt oil
  - Sed A, 21% dwt, density 1.18
  - Sed B, 65% dwt, density 1.71
- Amount of oil in test beaker varies considerably
  - Sed A = 24.8 mg oil / 100 ml sediment
  - Sed B = 111.1 mg oil / 100 ml sediment

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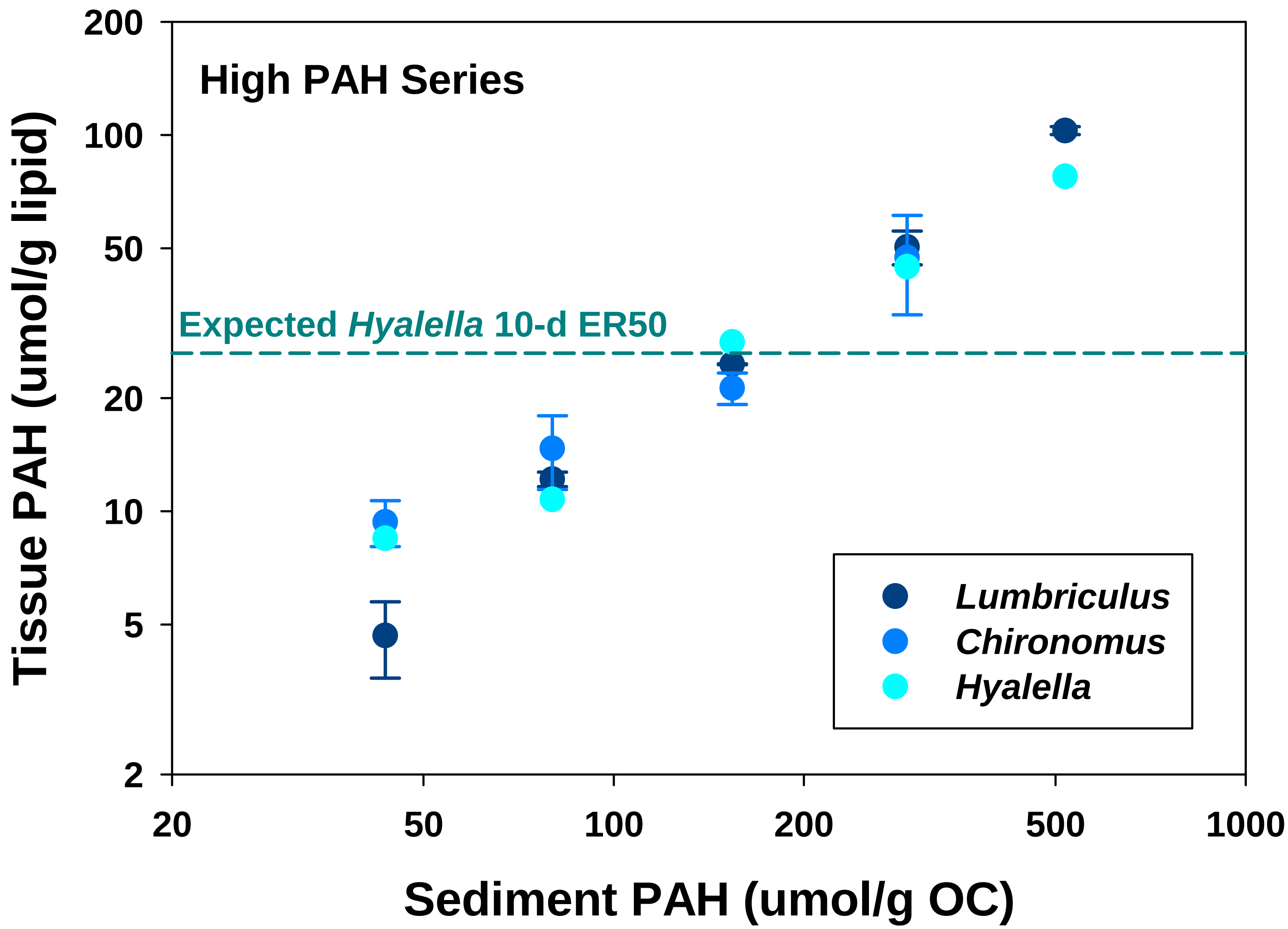
So Which is More Important, PAH or Oil Effects?

- Prepared three oils:
  - Mineral oil only (MO Only)
  - Mineral oil + 11% by mass PAH mixture (“Low PAH”)
  - Mineral oil + 32% by mass PAH mixture (“High PAH”)
- Spiked each oil into clean sediment at a range of concentrations and equilibrated
  - 0.25, 0.5, 1, 2, and 4 g/kg dwt
- Compared exposure/response among oils and organisms

Similar Uptake Across Species



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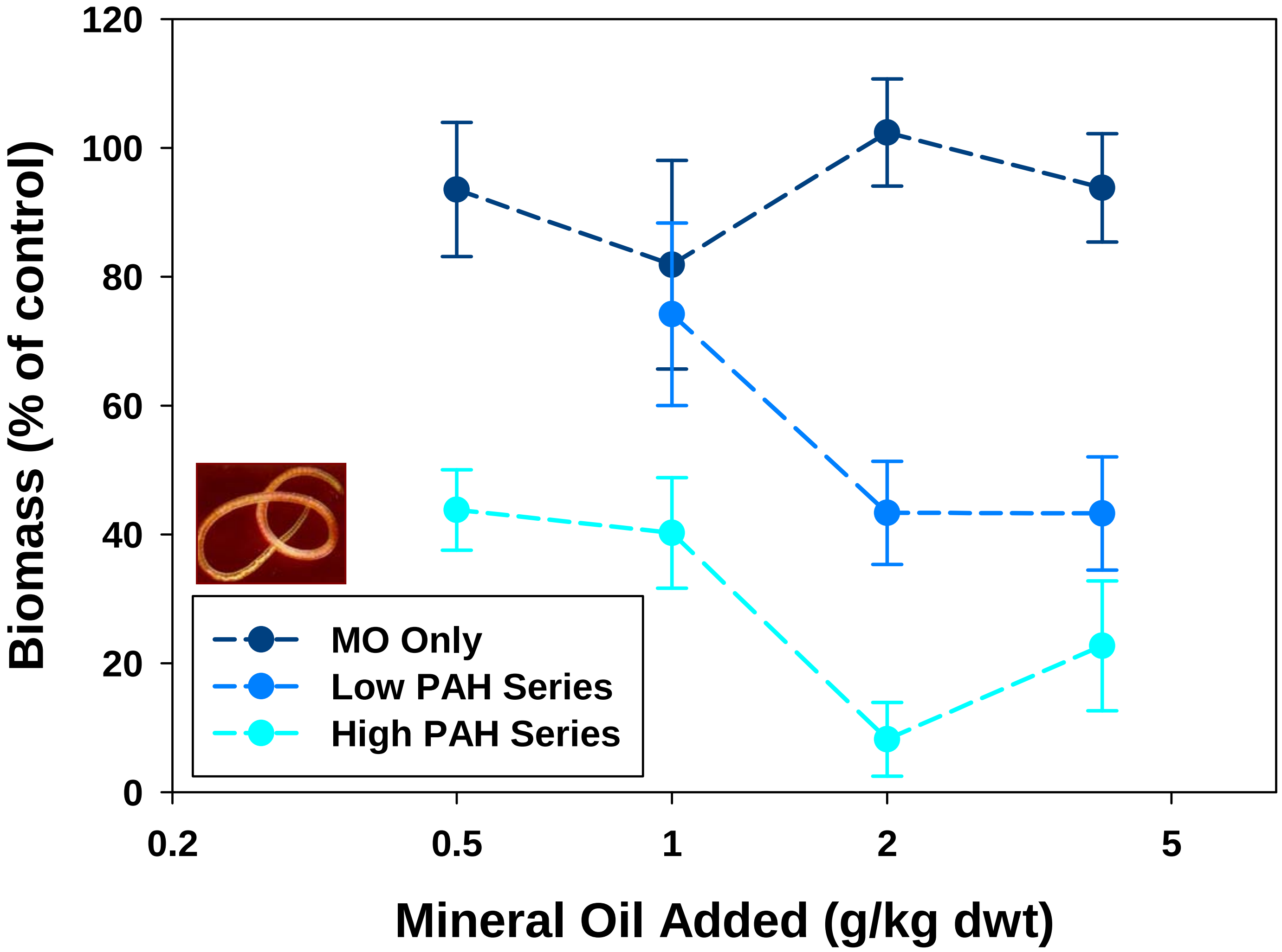
Lumbriculus



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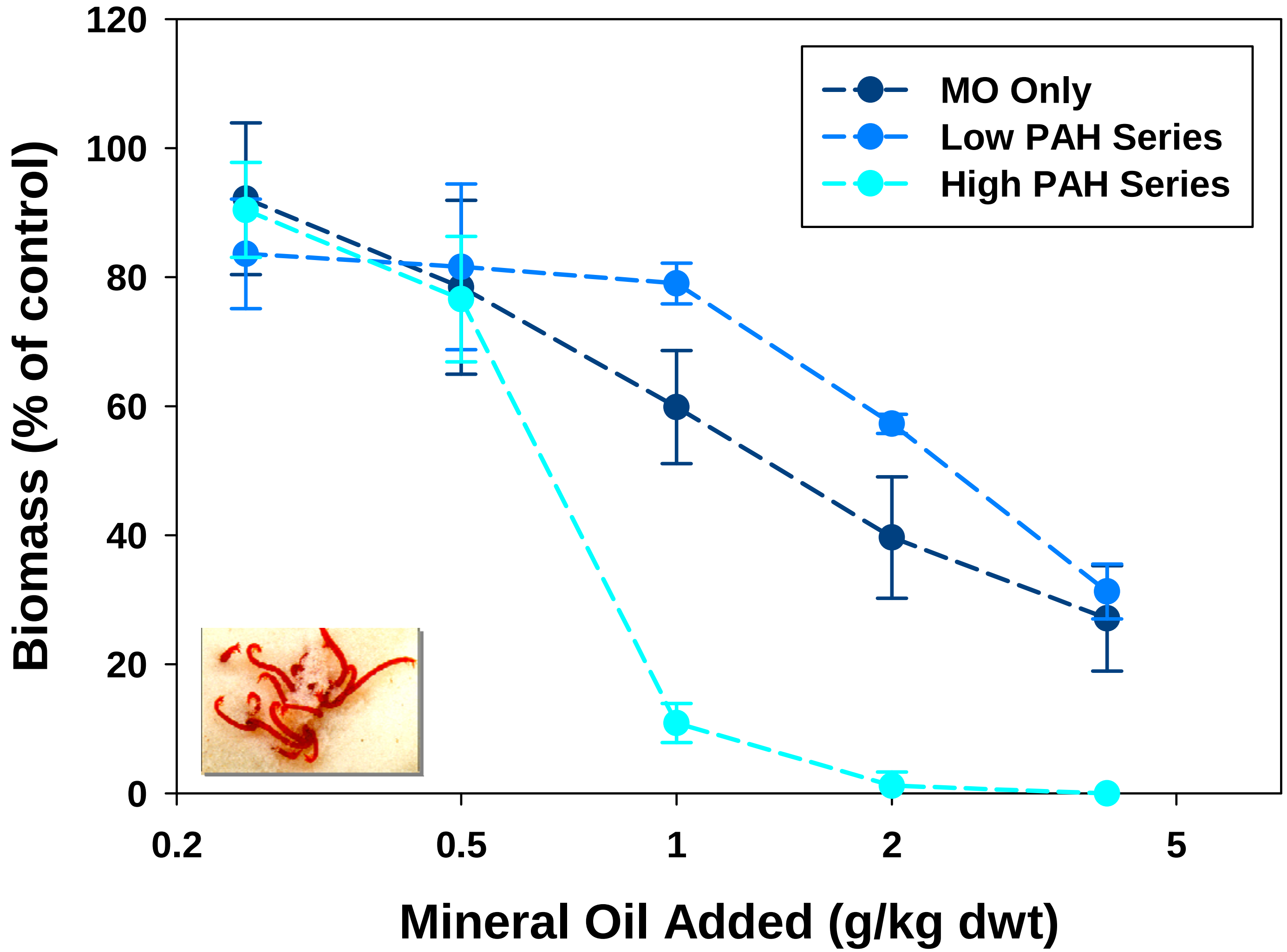
Chironomus



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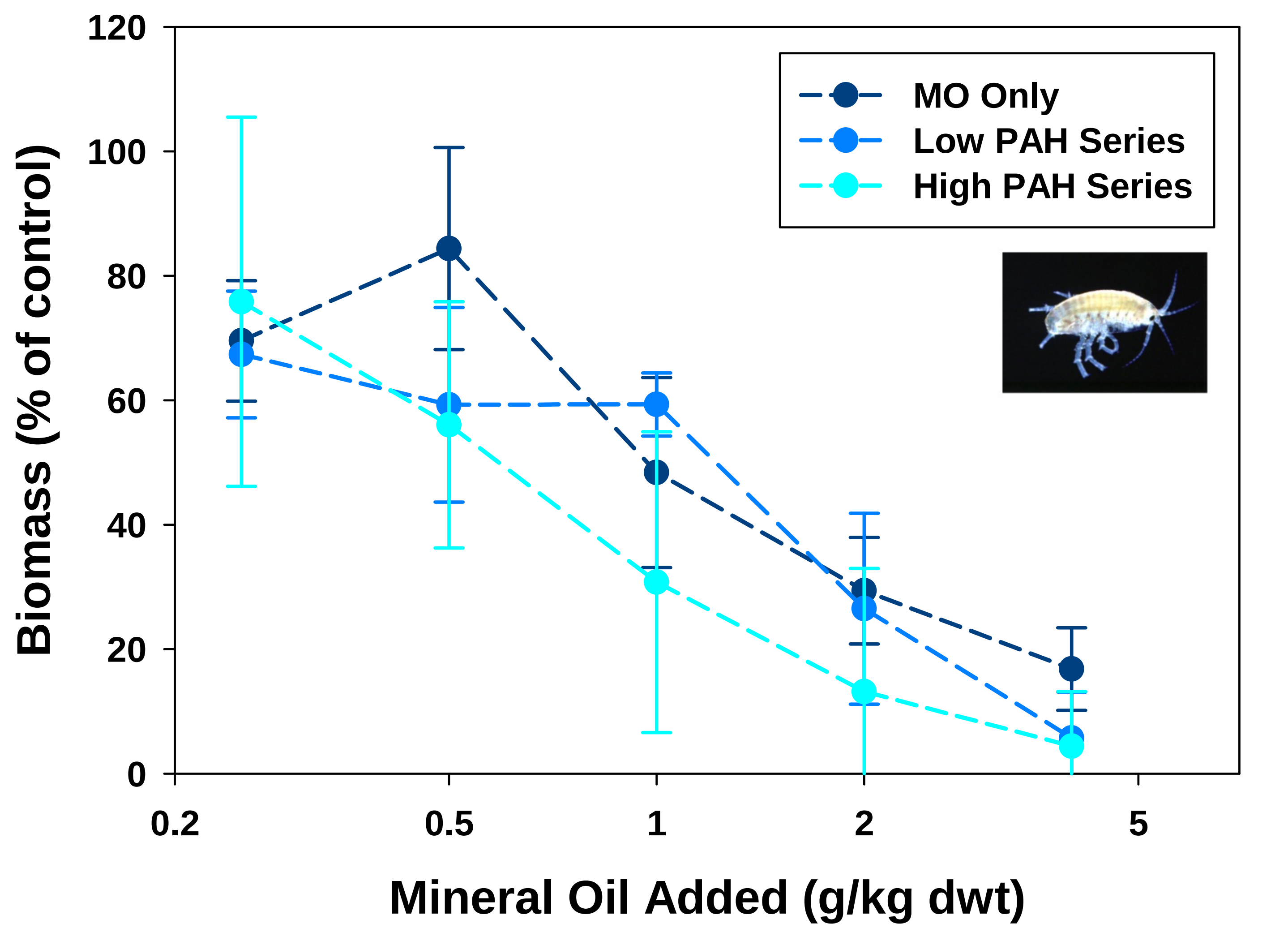
Hyalella



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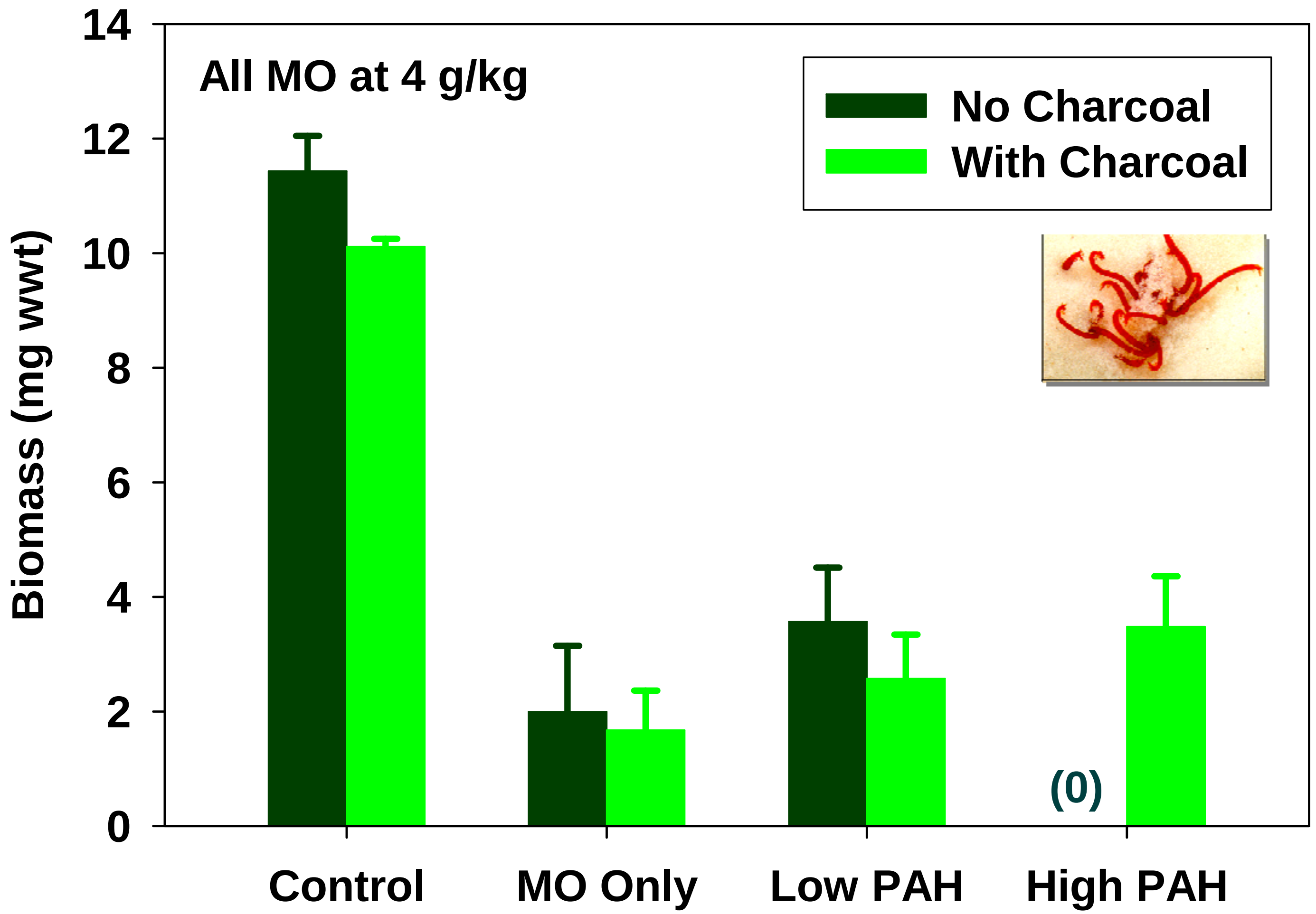
Effect of Charcoal: *Chironomus*



Estuarine Organisms

- Have tested sensitivity of some estuarine organisms to mineral oil
- *Ampelisca* (Rob Burgess, EPA-Narragansett)
  - 10-d LC50 = 20 g/kg
- *Leptocheirus* (Al Kennedy/Jacob Stanley ACOE-Vicksburg)
  - 10-d LC50 = 0.21 g/kg
- *Neanthes* (Al Kennedy/Jacob Stanley ACOE-Vicksburg)
  - 28-d NOEC > 18.75 g/kg
- Oil effect should be very important for *Leptocheirus* even more so than *Hyalella*

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Implications/Future Directions

- Convincing case that "oil" in sediment has an effect on some invertebrates beyond that from PAHs alone
- For oil-sensitive species, PAHs may drive effects only for NAPLs with very high PAH content (e.g., 30%)
- Looking at only PAHs may miss some types of oil contamination (e.g., lubricating oils)
- Normalization to volume appears important
- Differential response with/without charcoal may help parse effects of "oil" v PAHs
- Strong implications for estuarine sediment assessment
- Need a measure of "oil" that relates to "physical toxicity"

Implications for Dredged Material Evaluation

- "Mineral oil" effect may be more important than PAHs for some organisms
- *Leptocheirus* appears to be sensitive to both PAHs and "MO effect"
- SPME IW PAH_{34} measurement likely to be most accurate in flagging true PAH issues
- Assessment should include chemical measurements related to "MO effect"
  - oil and grease, DRO, RRO, TPH