Development of Porewater Remediation Goals (PWRGs) for the Protection of Benthic Organisms

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Introduction

- Development of Porewater Remediation Goals (PWRGs) for the Protection of Benthic Organisms
  - EPA 600/R-15/289 October 2017

Introduction

- OLEM-OSRTI requested this guidance
  - Numerous stakeholders
    - Asking for the incorporation of bioavailability measures into developing remedial goals
    - Techniques are available for assessing bioavailability

- Results (Potentially)
  - Simpler/less aggressive remedial designs
    - Remediate only the portion of the chemical causing the risk at the site
  - Lower remedial costs
  - Quicker completion of remedial actions

PWRG Methodology

- Methodology applicable to
  - Protection of benthic organisms from direct toxicity from sediment contaminants
  - Applicable to nonpolar organic chemicals
    - PAHs, chlorinated benzenes, pesticides …
- Methodology not applicable to
  - Effects resulting from bioaccumulation via the food chain
    - PCBs & PCDD/PCDFs
  - Higher trophic level benthic species
    - Crab, lobster, catfish, carp
  - Pelagic species
  - Cationic metals (Cu, Cd, Zn, Pb, Ni, Ag) & polar organics
    - Passive samplers in different stage of development

BACKGROUND

Background

- Need for thresholds for contaminants in sediments
  - Unacceptable risks
- Initial approaches → Empirical (pre-2000s)
  - Ignore bioavailability considerations
- Factors influencing sediment toxicity
  - Metals → sulfide
  - Organics → organic carbon
- Development of Equilibrium Partitioning Sediment Benchmarks (ESBs) (2000s)

Background

- ESBs based upon EqP theory
  - EqP asserts:
    - All phases in sediment are at equilibrium with each other
    - Bioavailability directly proportional to the chemical's activity
    - Chemical activity is the same in all sediment phases
    - C_{free} in pore water: good estimate of chemical activity
  - Bioavailable chemical = C_{free} in pore water
- ESBs developed in 2000s because
  - Methods for measuring C_{free} in pore water
    - Unavailable, many artifacts & biases

Background

- Equilibrium Partitioning Sediment Benchmarks (ESBs, µg/g-oc)
  - ESB is same for all sites
  - Adjusted for site-specific sediment organic carbon content → bulk concentrations (µg/kg-dw)

- ES

Final Chronic Value From EPA's AWQC

- K $\log K\downarrow OW$

Generic estimate of K_{OC}

Background

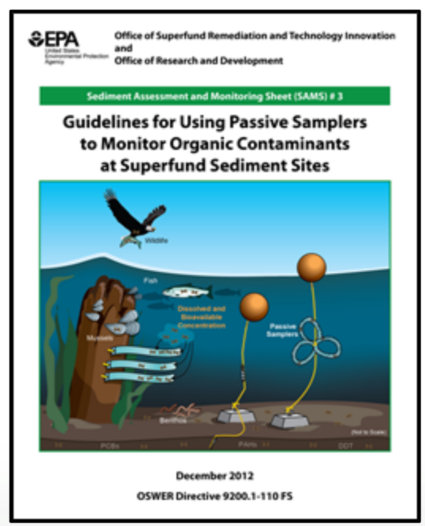
- Theoretical underpinning of ESBs strong!
- Not all "organic carbon" in sediments is the "same"
    - Variety of diagenic, petrogenic, and pyrogenic forms
    - K_{OC} values vary across different carbon types
    - K_{OC} values vary within and across sites
- ESBs
    - Diagenic organic carbon-water partitioning
    - K_{OC} values lower $\rightarrow$ more chemical being bioavailable

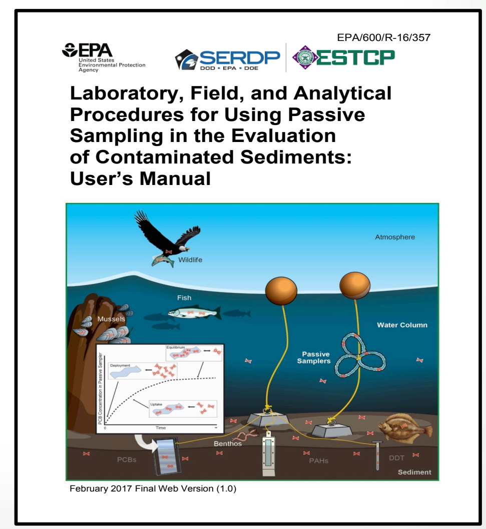
Background

- With development of passive sampling
  - C_{free} in porewater can be measured
    - Measure of chemical activity
    - Measure of chemical bioavailability in sediments
      - Bioavailable chemical = C_{free} in pore water

Background

- Guidance approach
  - Two basic elements
    - Method of measuring/inferring freely dissolved chemical concentrations in sediment pore water
    - Threshold chemical concentrations that delineates acceptable and unacceptable exposures



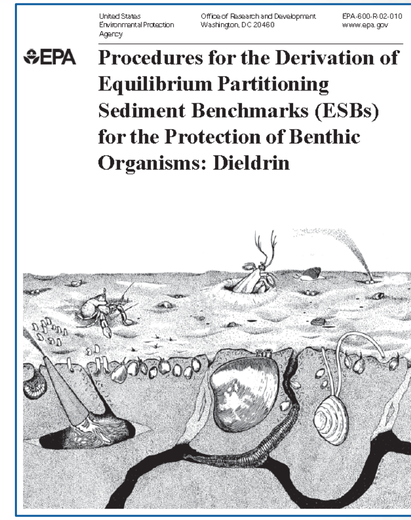


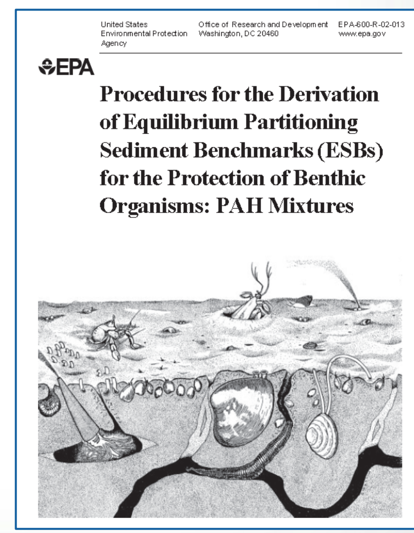
Final Chronic Values

Thresholds for Acceptable/Unacceptable

Acceptable and Unacceptable Exposure Thresholds

- EPA's Equilibrium Sediment Benchmarks
  - Final Chronic Value (FCV) from EPA's Ambient Water Quality Criterion (AWQC) for aquatic life is exposure threshold
  - Secondary Chronic Values (SCV)
    - Derived using Great Lakes Water Quality Initiative methodology
    - For chemicals without FCVs





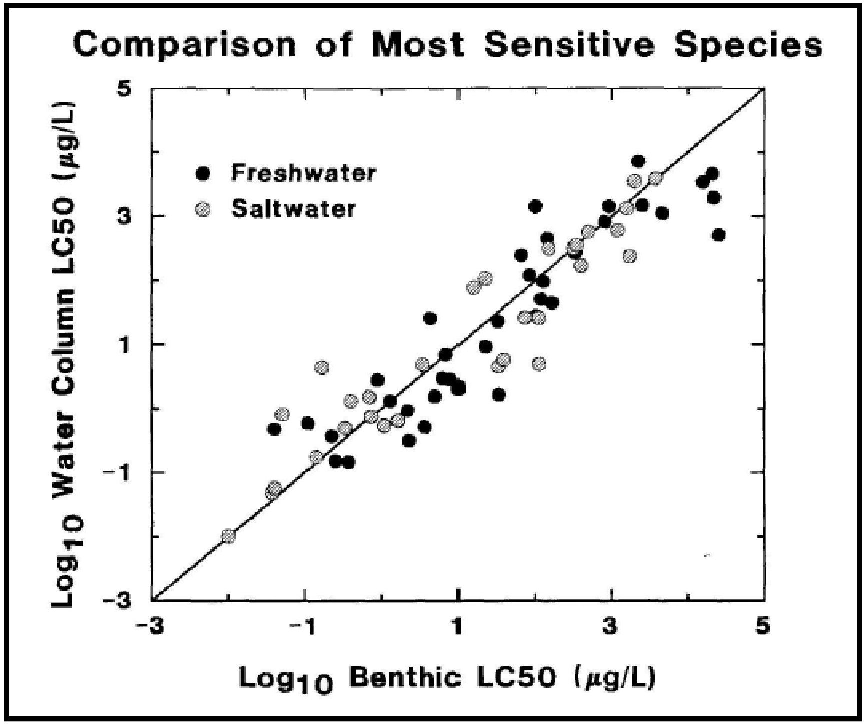
- PWRG methodology uses
  - Final Chronic Values (FCVs)
  - Secondary Chronic Values (SCVs)

Acceptable and Unacceptable Exposure Thresholds

- FCVs and SCVs
  - Derived using toxicity sensitivity distributions with benthic and pelagic organisms
  - 5th percentile from the Species Sensitivity Distribution

- Logical question:
  - Are benthic organisms consistently more or less sensitive to chemical toxicants than are pelagic organisms?

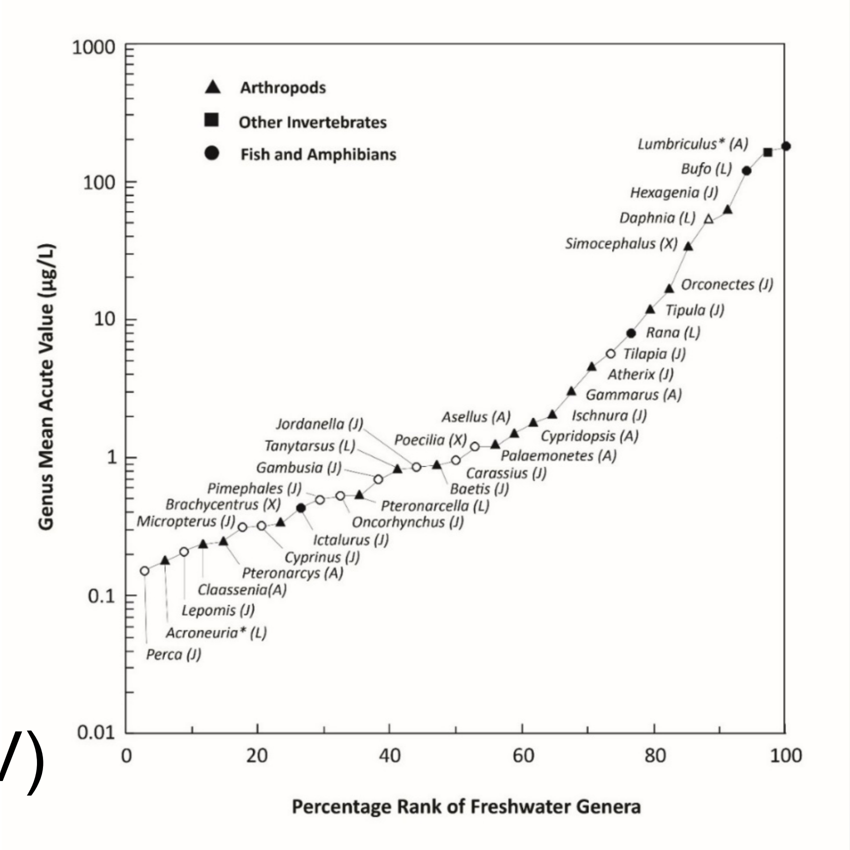
Acceptable and Unacceptable Exposure Thresholds



- Comparison of the minimum LC50 for infaunal and epibenthic species (X-axis) and water column species (Y-axis). Data from AWQC or draft AWQC documents (Di Toro et al. 1991)

Acceptable and Unacceptable Exposure Thresholds

- Species sensitivity distribution for Endrin
  - Freshwater species
- Final Acute Value (FAV)
  - 0.1803 µg/L
- Final Acute to Chronic Ratio (FACR)
  - 3.106
- Final Chronic Value (FCV)
  - 0.05805 µg/L

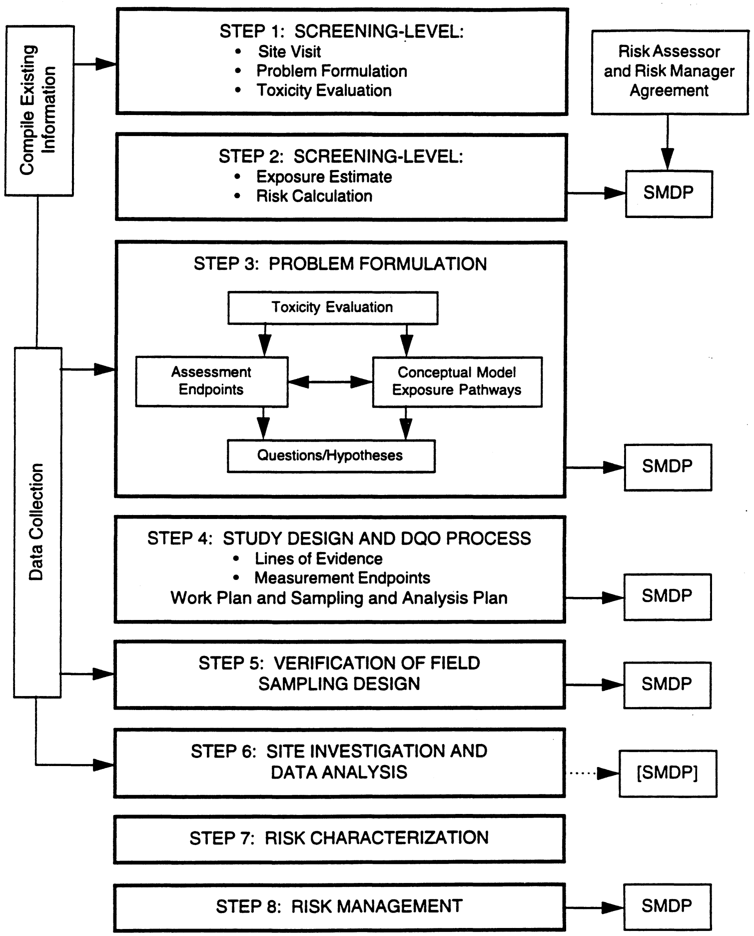


PWRG Methodology

PWRG Methodology

- Suggested Methodology Developing PWRGs
  - Follows Superfund's eight-step ERA guidance

EXHIBIT I-2
Eight-step Ecological Risk Assessment Process for Superfund



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PWRG Methodology

- **Screening Level Characterization of the Nature and Extent of Contamination**
  1) Measure f_{OC} and C_S for all COCs (µg/kg-dw) in surficial sediments across the site
  2) Compute C_{SOC} (µg/kg-OC) for all COCs
  3) Compute Toxic Units (TUs) for COCs
     - For single toxicant case, $TU = C_{SOC}/ESB$
     - For mixture of toxicants,
       - For each COC: $TU_i = C_{SOC,i}/ESB_i$
       - Total $TUs = \sum TU_i$

Step 1:
Screening Level

Step 2:
Screening Level

Step 3:
Problem Formulation

Step 4:
Study Design
&
DQO Process

Step 5:
Field Ve ification

Step 6:
Site Investigation
&
Exposure Analysis

Step 7:
Risk Characterization

Step 8:
Risk Management

PWRG Methodology

- **Problem Formulation**
  - Develop CSM, exposure pathways, and assessment endpoints
- **Study Design and DQO Process**
  - Develop Work Plan (WP) and Sampling and Analysis Plan (SAP) in support of CSM and data needs

Step 1:
Screening Level

Step 2:
Screening Level

**Step 3:
Problem Formulation**

**Step 4:
Study Design
&
DQO Process**

Step 5:
Field Ve ification

Step 6:
Site Investigation
&
Exposure Analysis

Step 7:
Risk Characterization

Step 8:
Risk Management

PWRG Methodology

- **Site Investigation and Data Analysis**
  4) Passively sample surface sediments where total TUs > 1.0
  5) Derive C_{free} and K_{OC} values for surface sediments with total TUs > 1.0

- **Risk Characterization**

Step 1:
Screening Level

Step 2:
Screening Level

Step 3:
Problem Formulation

Step 4:
Study Design
&
DQO Process

Step 5:
Field Ve ification

Step 6:
Site Investigation
&
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Risk Management

PWRG Methodology

- **Baseline Ecological Risk Assessment**

6) Compute Toxic Units (TUs) for COCs
   - For single toxicant case, $PWTU = C_{free}/FCV$
   - For mixture of toxicants, for each COC in the mixture:
     - Compute pore water TU for each COC,
       $PWTU_i = C_{free,i}/FCV_i$
     - Compute total mixture pore water TUs,
       $PWTU_{Mixture} = \Sigma PWTU_i$

7) For locations where:
   - Total PWTUs ≤ 1.0, little potential for risk.
   - Total PWTUs > 1.0, unacceptable risks indicated
     - Proceed to Remedial Goal Development

Step 1: Screening Level

Step 2: Screening Level

Step 3: Problem Formulation

Step 4: Study Design & DQO Process

Step 5: Field Ve ification

Step 6: Site Investigation & Exposure Analysis

Step 7: Risk Characterization

Step 8: Risk Management

PWRG Methodology

Step 1:
Screening Level

Step 2:
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Remedial Goal Development

- PWRGs
  - $C_{free:PWRG}$ (µg/L)
  - Bulk sediment basis ($C_{S:PWRG}$ µg/kg dry weight)
  - OC basis ($C_{SOC:PWRG}$ µg/kg organic-carbon)

PWRG Methodology

- **Remedial Goal Development**

8b) PWRGs: bulk sediment basis ($C_{S:PWRG}$ µg/kg dry weight)

- Derive site specific $f_{OC:SS}$ and $K_{OC:SS}$ values
- $K_{OC:SS} = (C_S / f_{OC:SS}) / C_{free}$

a) PWRG for single toxicant:

$$C_{S:PWRG} = K_{OC:SS} \times f_{OC:SS} \times C_{free:PWRG}$$

where $C_{free:PWRG}$ = FCV

Step 1: Screening Level

Step 2: Screening Level

Step 3: Problem Formulation

Step 4: Study Design & DQO Process

Step 5: Field Ve ification

Step 6: Site Investigation & Exposure Analysis

Step 7: Risk Characterization

Step 8: Risk Management

PWRG Methodology

Remedial Goal Development

8b continued) PWRGs: bulk sediment basis ($C_{S:PWRG}$ µg/kg dry weight)

b) For mixture of toxicants:
- Individual components: compute $C_{S:PWRG,i}$
  - $C_{S:PWRG,i} = K_{OC:SS,i} \times f_{OC:SS,i} \times C_{free:PWRG,i}$
    where $C_{free:PWRG,i} = FCV_i \times PWTU_i / PWTU_{Mixture}$
- Sum components
  - $C_{S:PWRG,Mixture} = \Sigma C_{S:PWRG,i}$

Step 1: Screening Level

Step 2: Screening Level

Step 3: Problem Formulation

Step 4: Study Design & DQO Process

Step 5: Field Ve ification

Step 6: Site Investigation & Exposure Analysis

Step 7: Risk Characterization

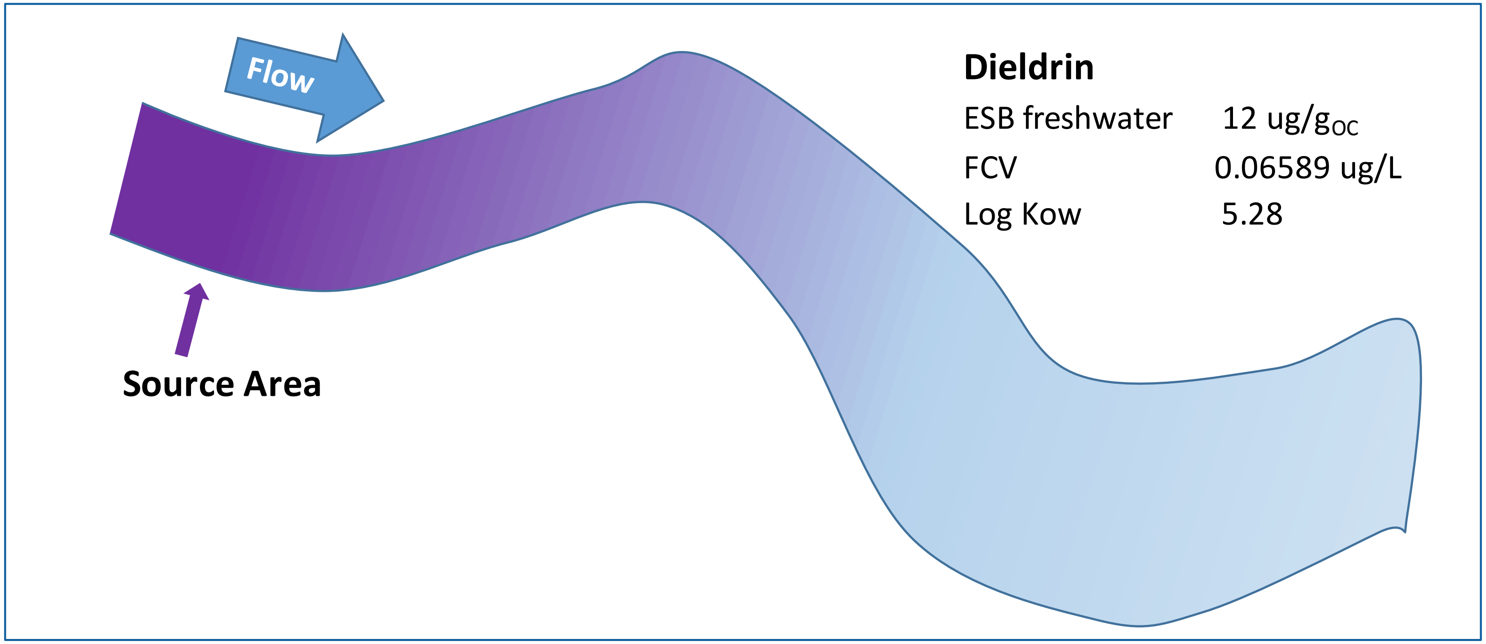
Step 8: Risk Management

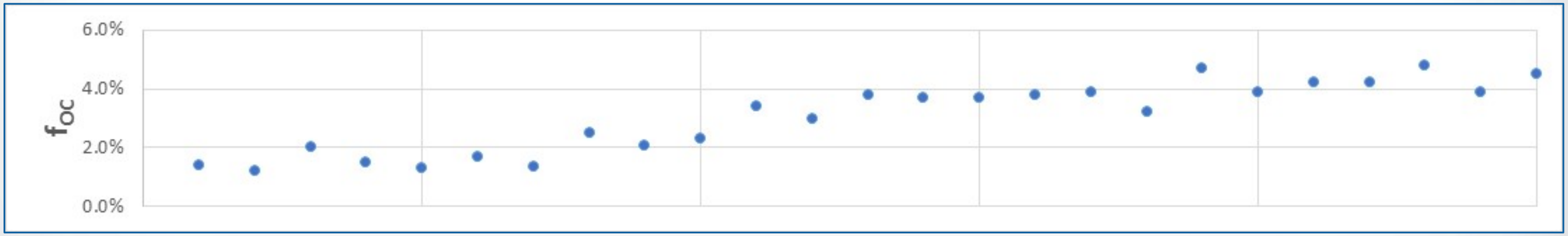
PWRG Methodology

- Step through illustrative example

PWRG Methodology

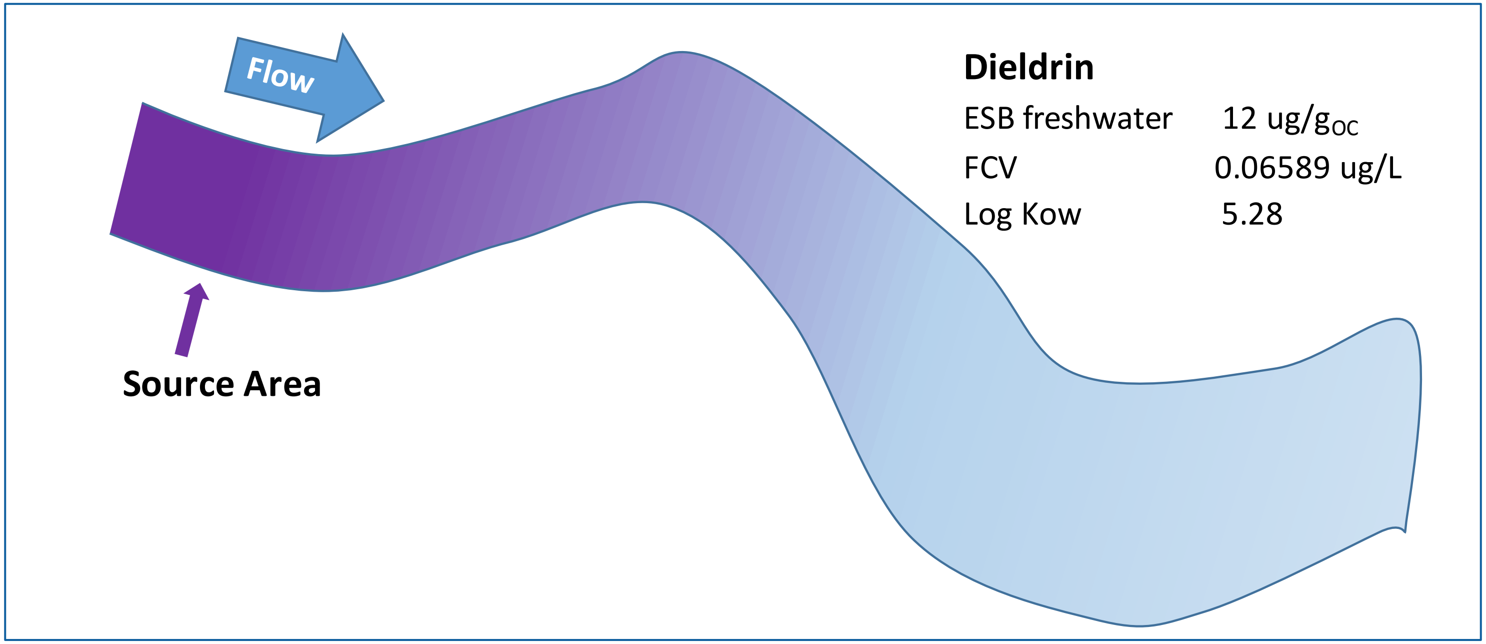
1) Measure f_{OC} (define nature and variability)

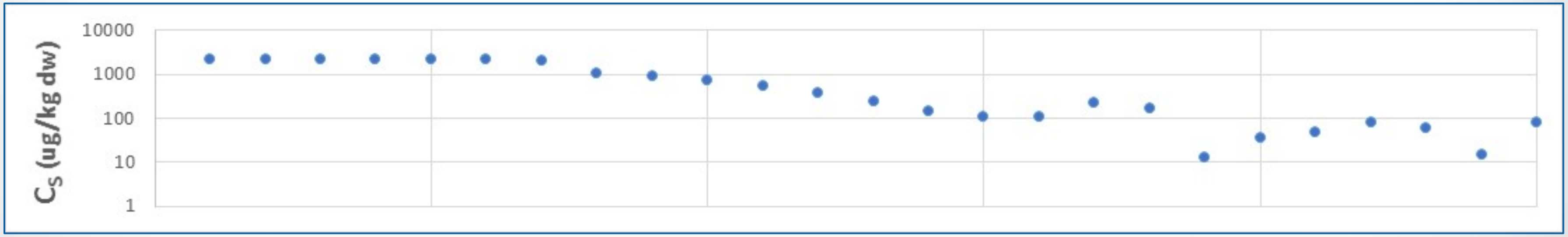




PWRG Methodology

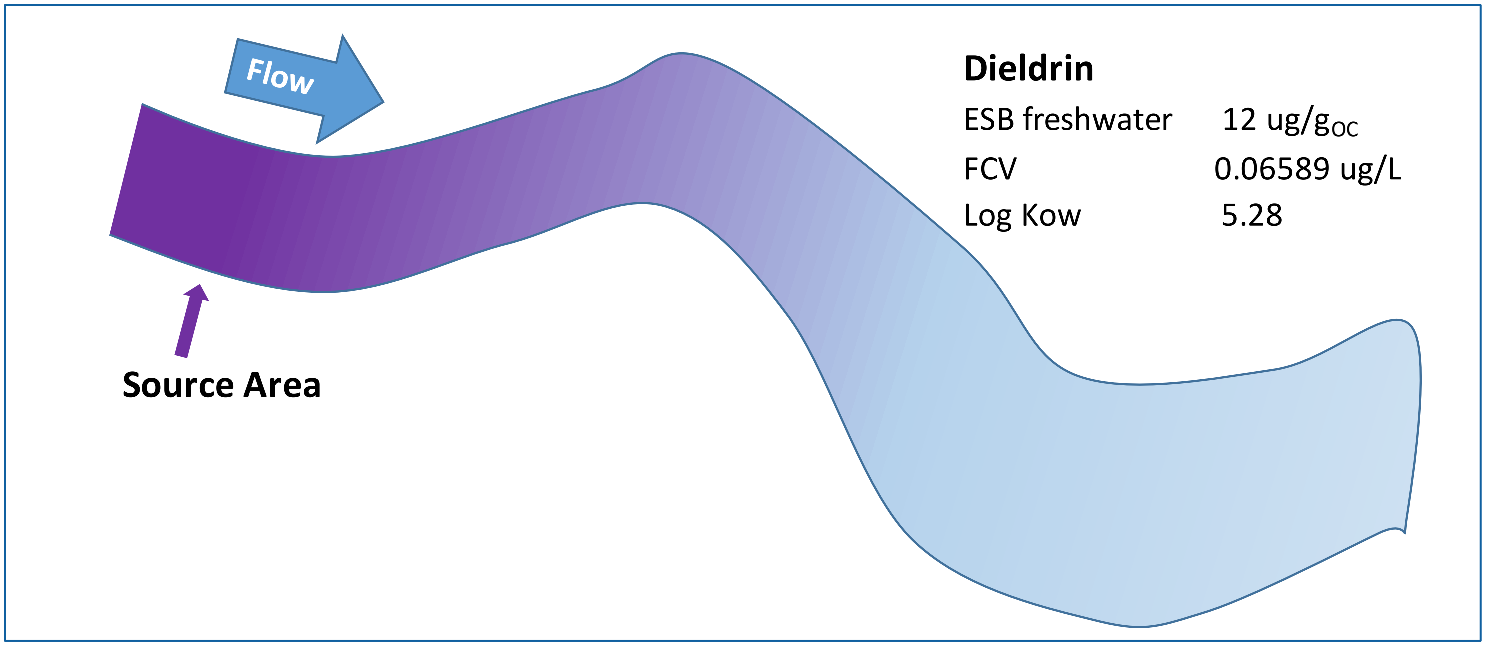
1) Measure $C_{sediment}$ (define nature and variability)

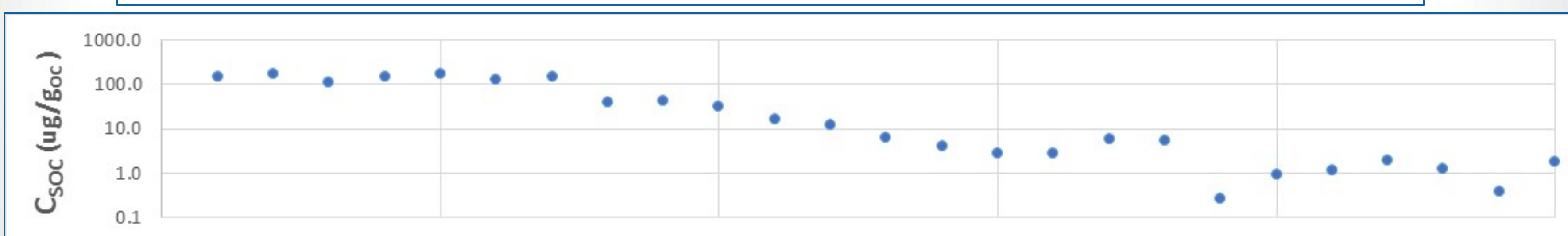




PWRG Methodology

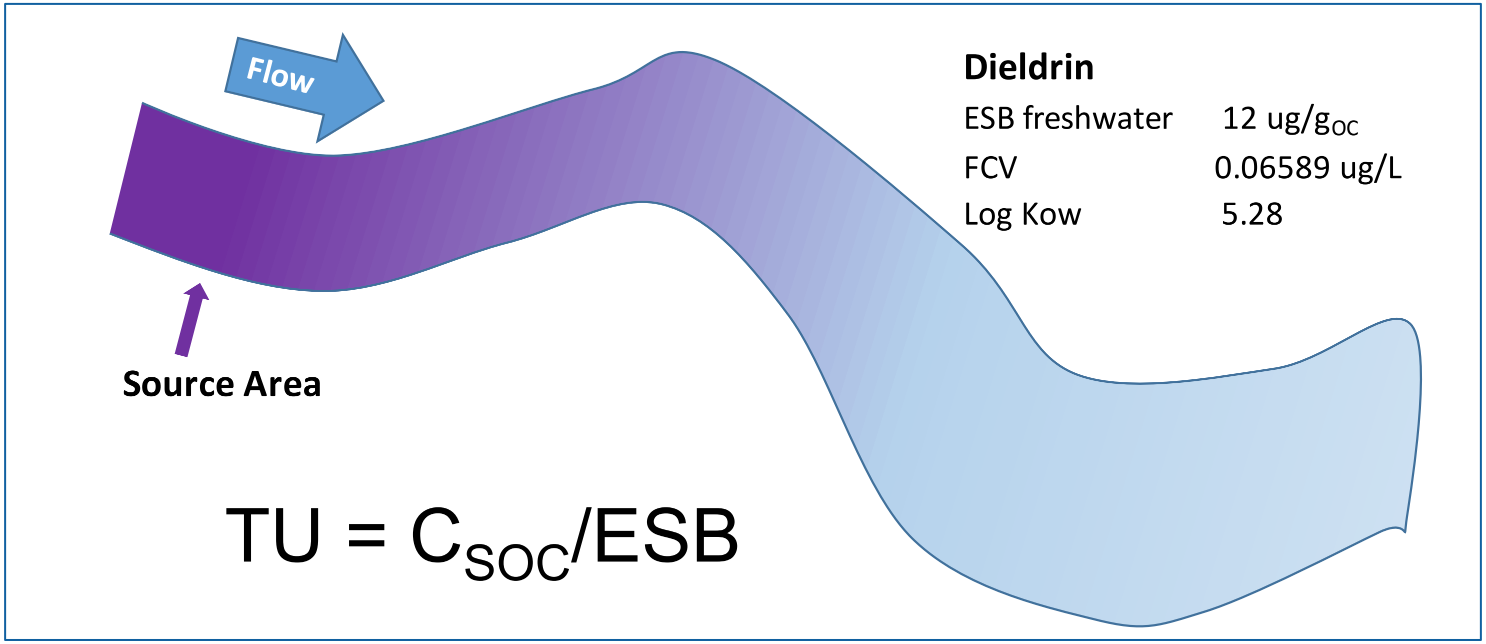
2) Determine C_{SOC} $\quad$ $C_{SOC} = C_{sediment}/f_{OC}$

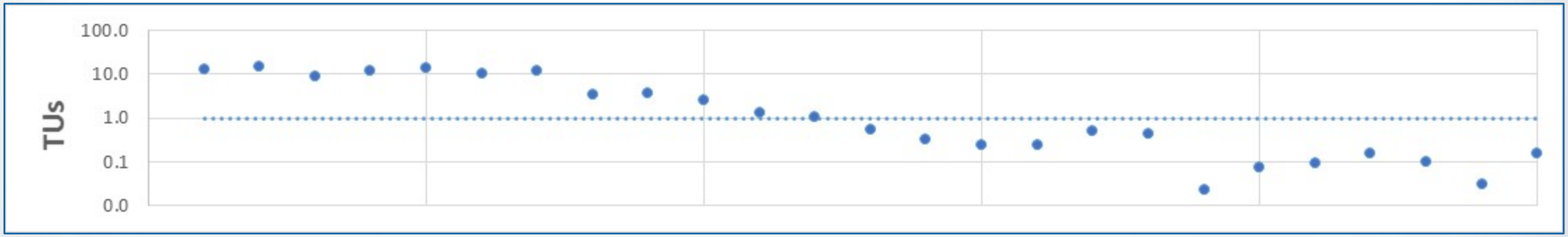




PWRG Methodology

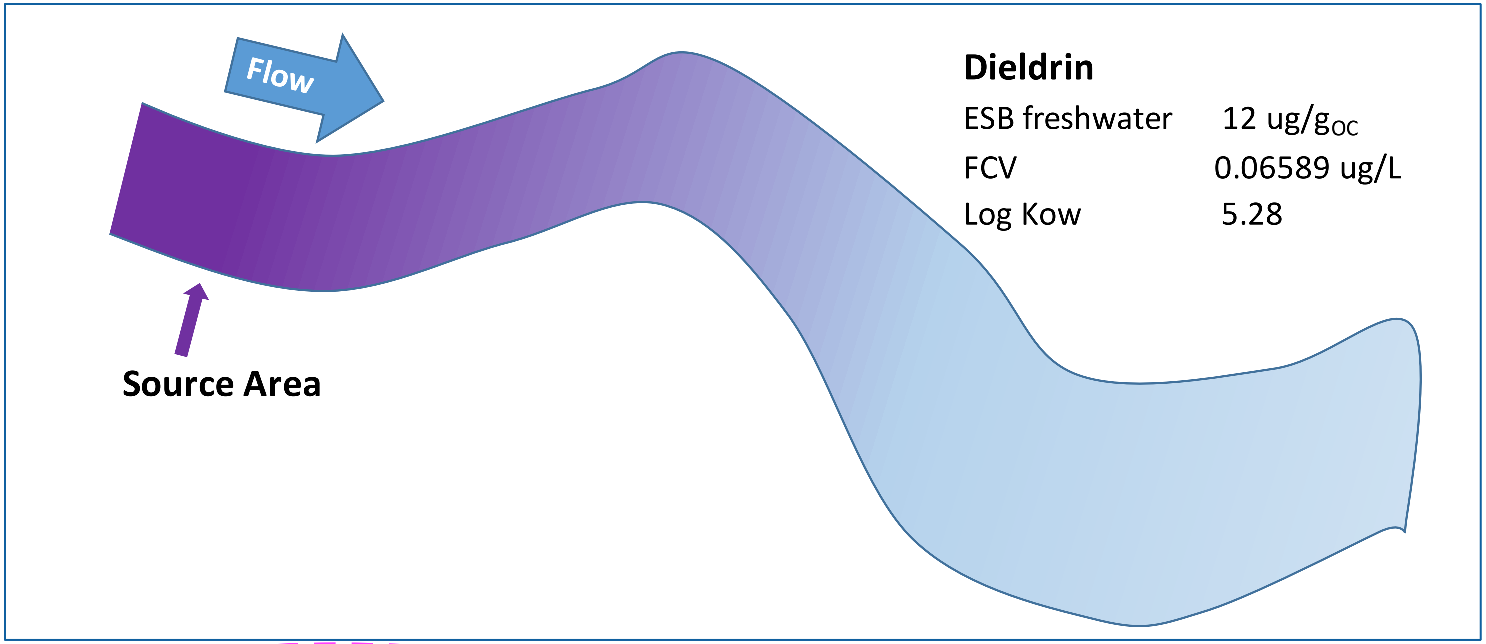
3) Compute Toxic Units (TUs) for Dieldrin

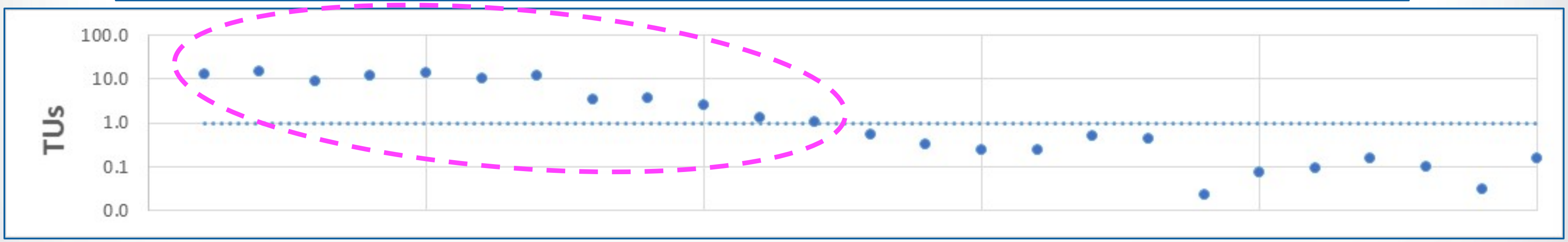




PWRG Methodology

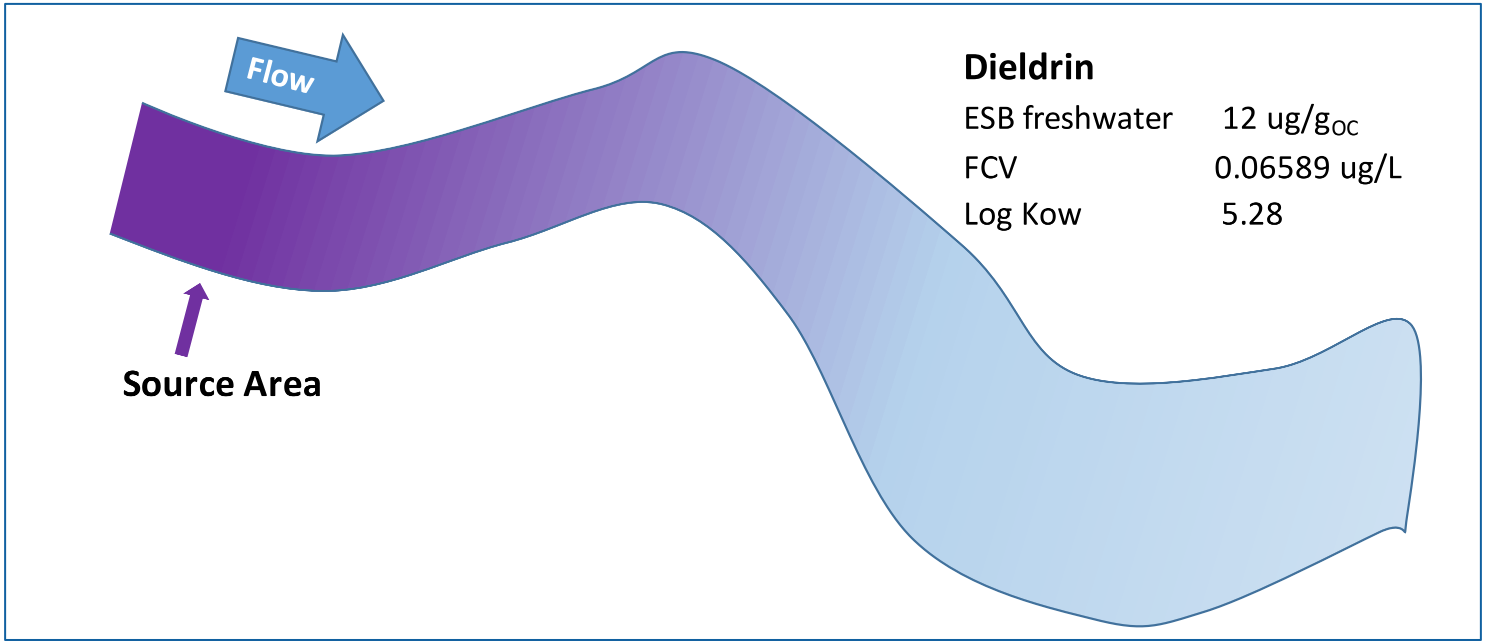
4) Passively sample sediments with TUs > 1.0

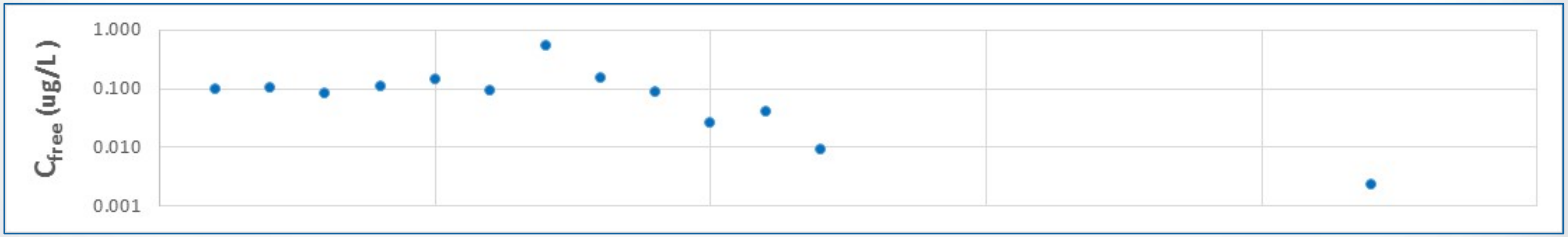




PWRG Methodology

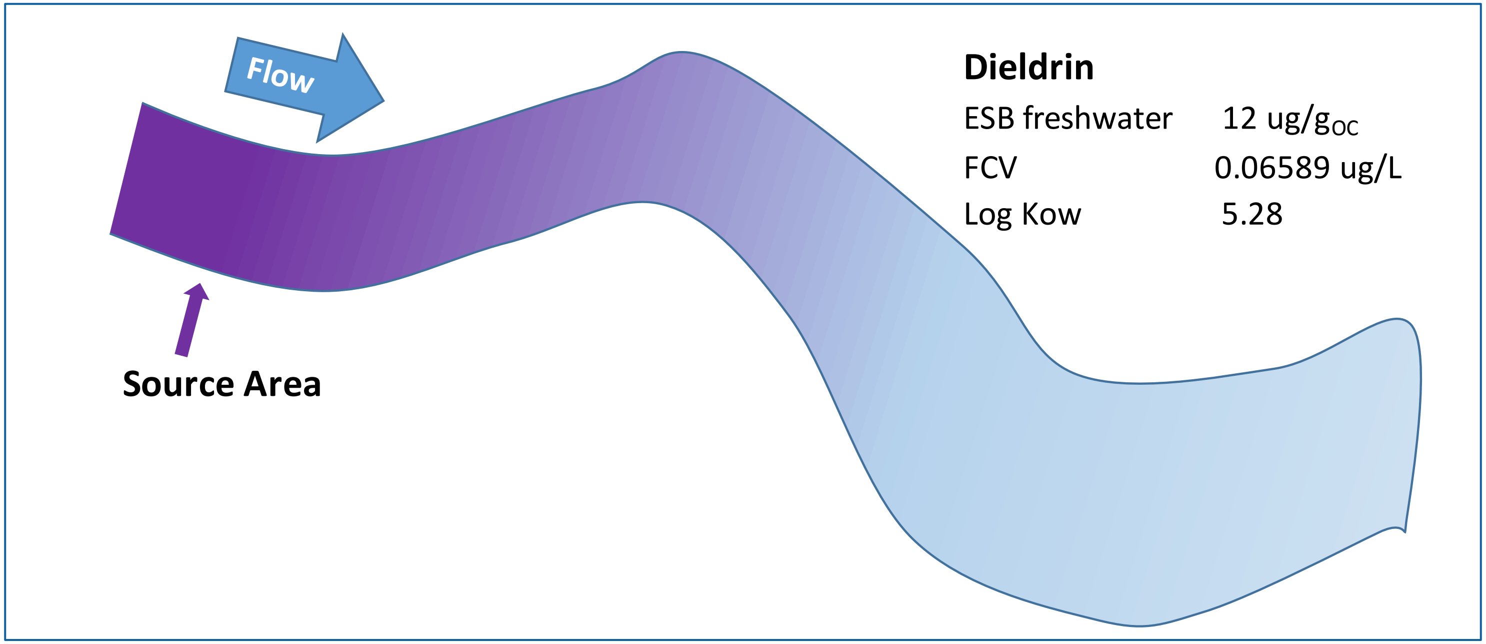
5) Measure C_{free} for sediments with TUs > 1.0

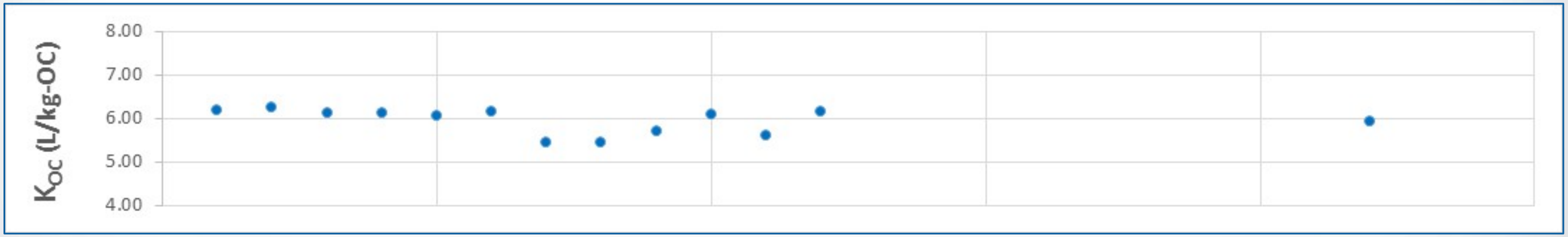




PWRG Methodology

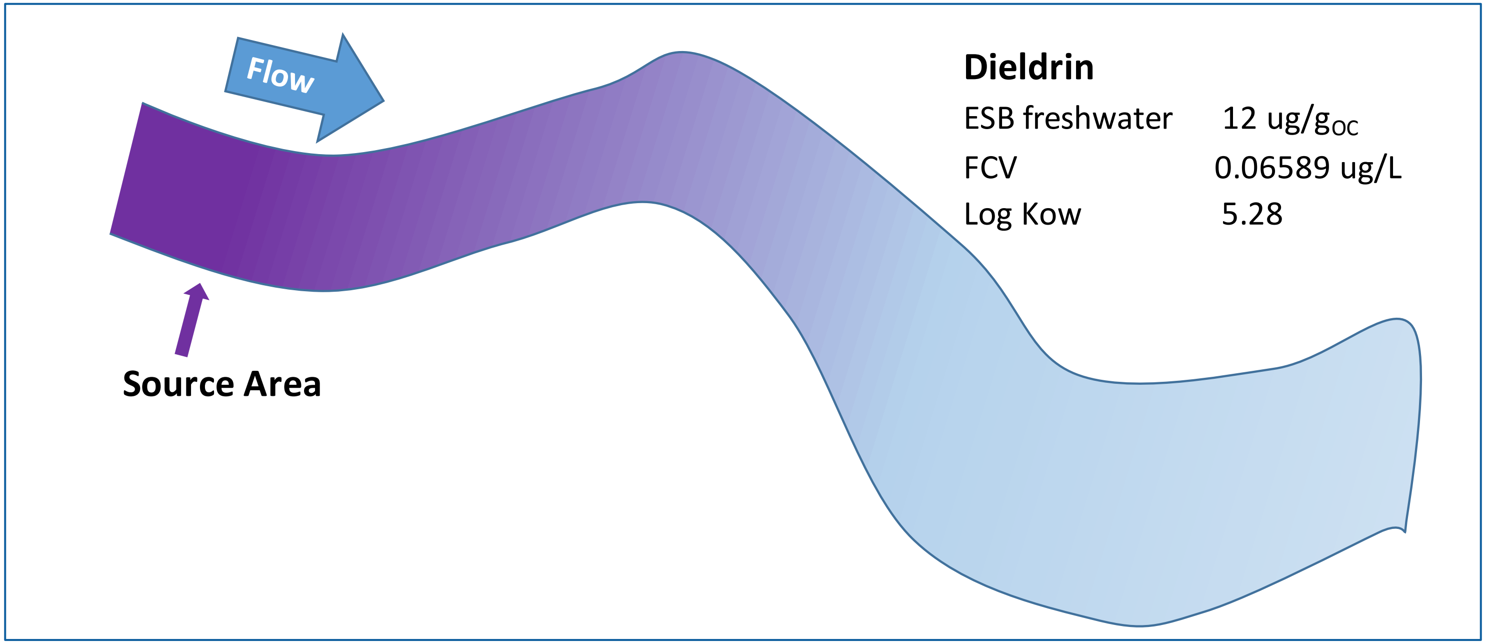
5) Measure K_{OC} for sediments with TUs > 1.0

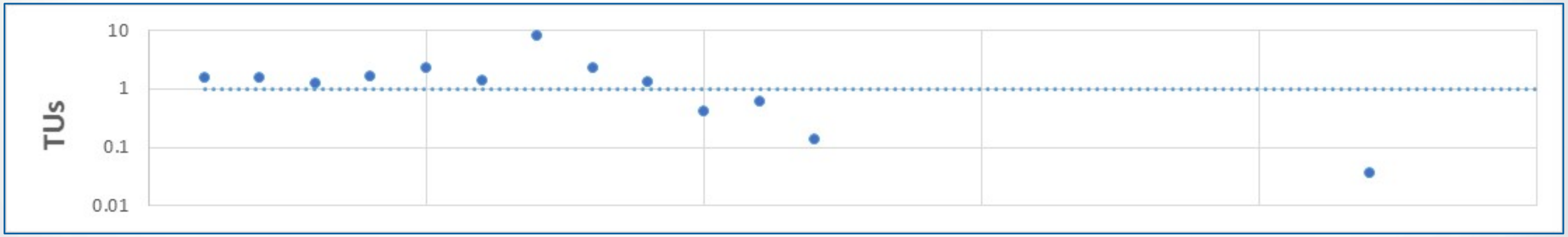




PWRG Methodology

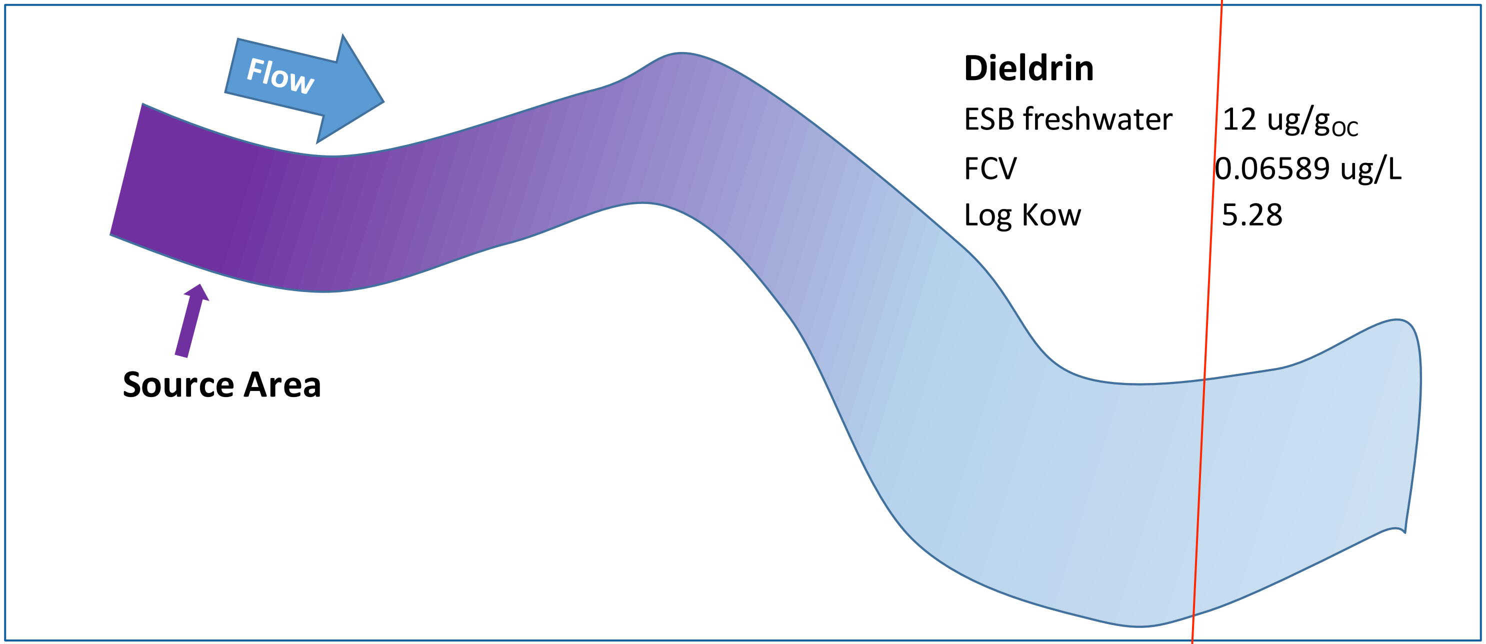
6) Compute TUs for Dieldrin $TU = C_{free}/FCV$

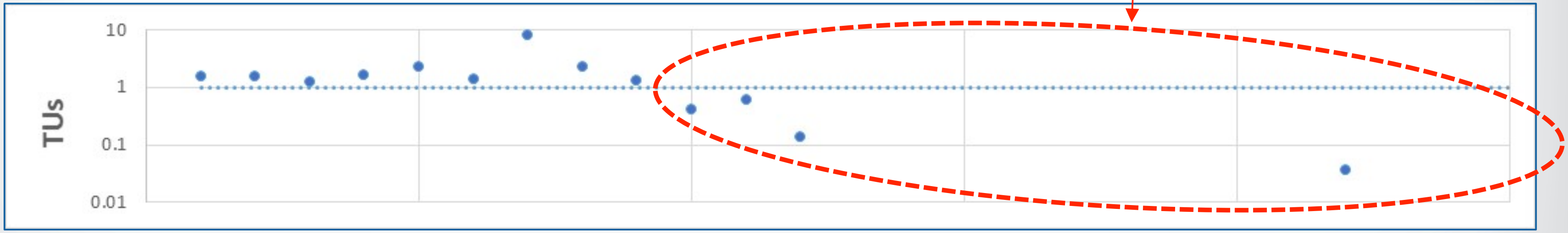




PWRG Methodology

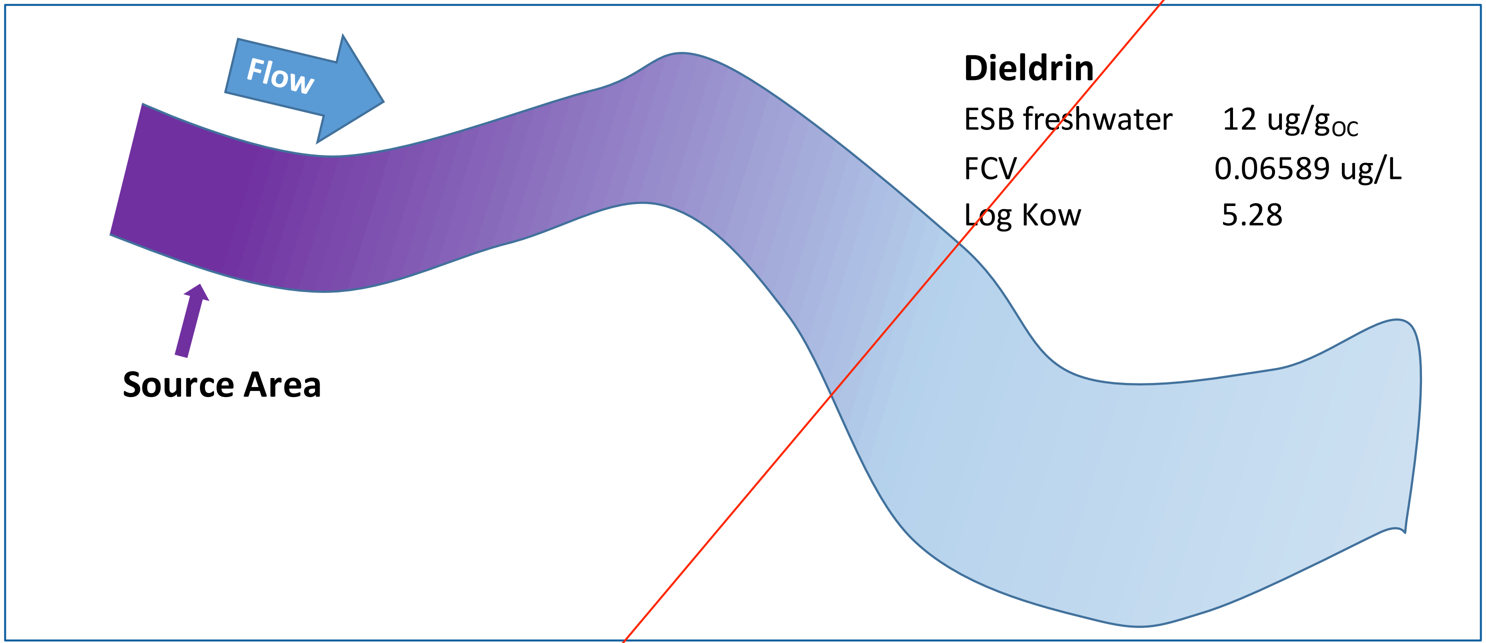
7) Total PWTUs ≤ 1.0: Little potential risk

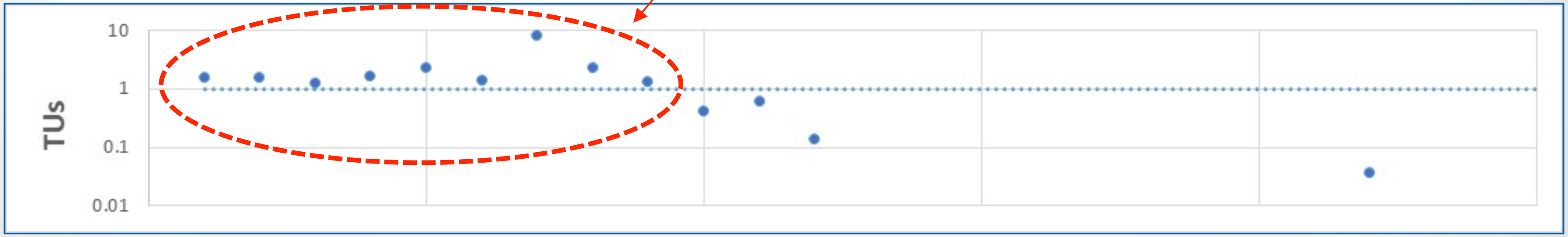




PWRG Methodology

7) Total PWTUs > 1.0: Unacceptable risks

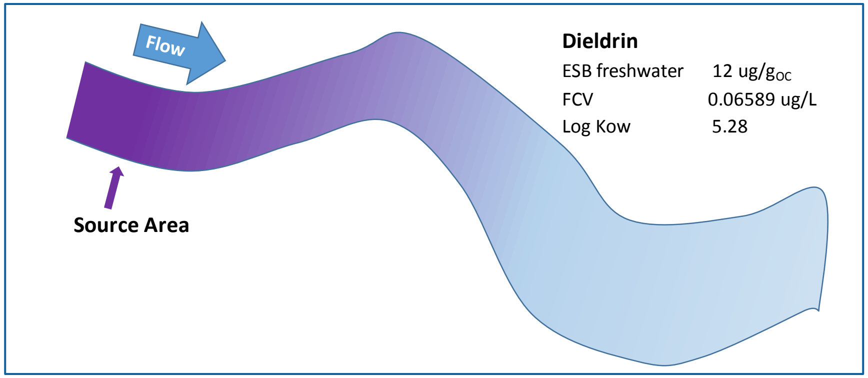




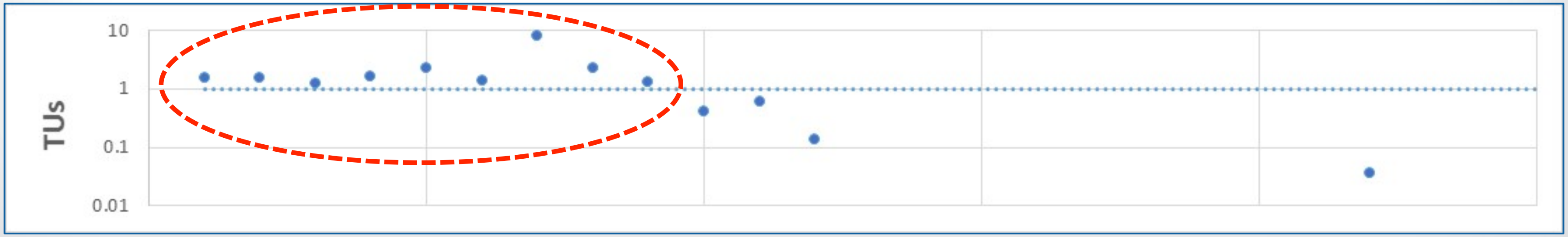
PWRG Methodology

8) Remedial Goal Development   3 options

- Concentration in:
  - Pore water — $C_{free:PWRG}$ (µg/L)
  - Bulk sediment — $C_{S:PWRG}$ (µg/kg-dw)
  - Sediment organic carbon basis — $C_{SOC:PWRG}$ (µg/kg-oc)



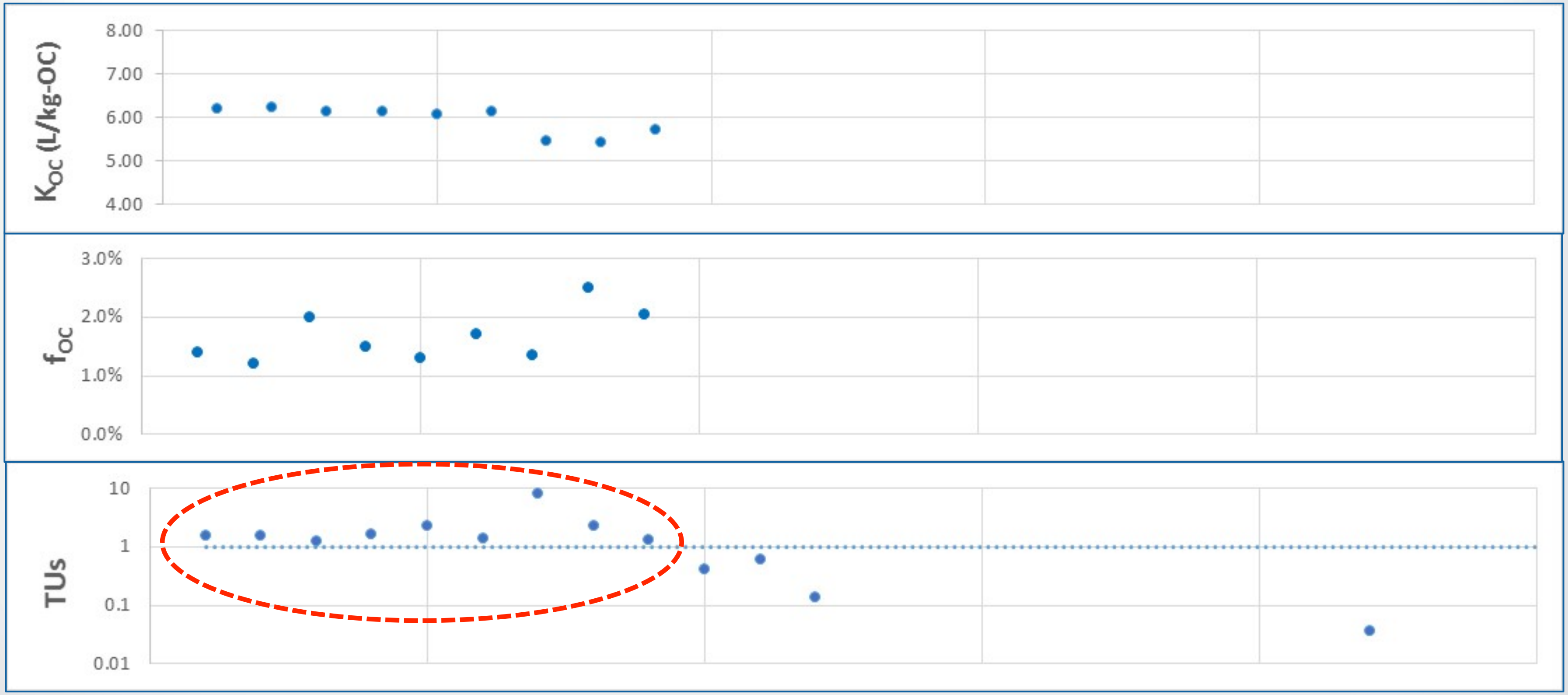
Project team will need to select an option!



PWRG Methodology

8) Remedial Goal Development

- Focus on bulk sediment option: $C_{S:PWRG}$ (µg/kg dw)
- $C_{S:PWRG} = K_{OC:SS} \times f_{OC:SS} \times C_{free:PWRG}$



PWRG Methodology

8) Remedial Goal Development

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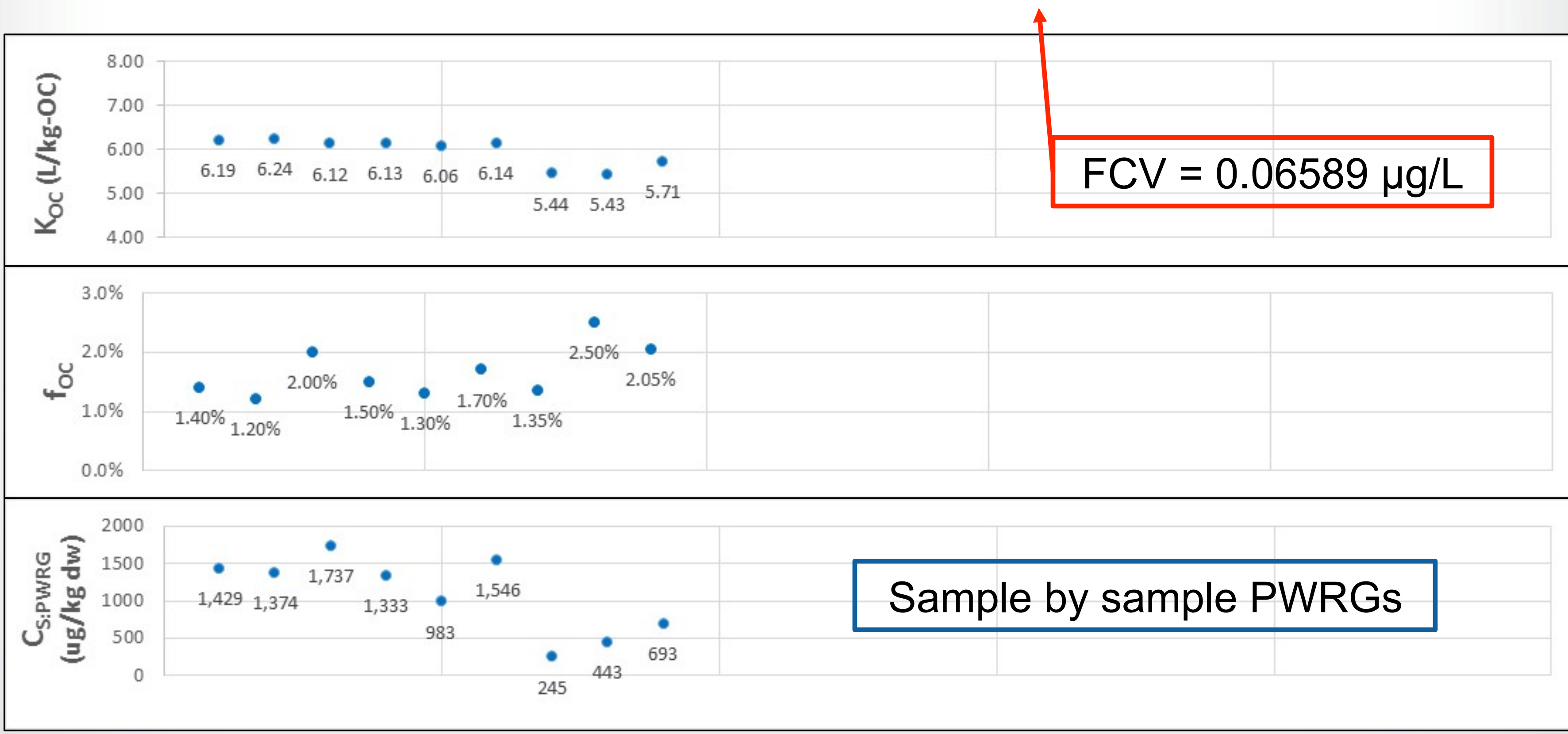


PWRG Methodology

8) Remedial Goal Development

- Bulk sediment option: $C_{S:PWRG}$ (µg/kg dw)
- $C_{S:PWRG} = K_{OC:SS} \times f_{OC:SS} \times C_{free:PWRG}$

- Sample by sample PWRG development
  - Not realistic
  - Not enough data

- For your site: Develop site $K_{OC:SS}$ and $f_{OC:SS}$
  - Central tendency value for $K_{OC:SS}$ and $f_{OC:SS}$
    - mean or median
    - Use 95% UCL as RME
    - Define by OUs, sub-areas … of the site?

PWRG Methodology

8) Remedial Goal Development

- $K_{OC:SS}$ and $f_{OC:SS}$ development

- If low variability
  - Selecting a single value should be straight forwards
- If high variability
  - Will require some work to determine appropriate values
    - » Spatial patterns
    - » Site history and knowledge may allow parsing of the variability
    - » Distribution of the values
    - » Subdividing the site

PWRG Methodology

8) Remedial Goal Development

- $K_{OC:SS}$ and $f_{OC:SS}$ development

- How many passive sampling measurements are enough for a site?
  - Site specific decision
    - 1 or 2 samples clearly not enough
    - Measure bulk and C_{free} concentrations on all sediments too expensive
    - Depends upon expect variance
      - » Use power analysis to estimate sample numbers

- What samples should be done?
  - Surface sediments

Mixtures: PWRG Methodology

- Must use Toxic Units (TUs)
  - Individual components

$$PWTU_i = C_{free,i} / FCV_i$$

  - Mixture

$$PWTU_{Mixture} = \sum_{i=1}^{j} PWTU_i$$

Mixtures: PWRG Methodology

Table 4-3. Example calculation of pore water toxicity and PWRGs for a sediment with a PAH Mixture as the known toxicants.

	<u>Measured Concentration</u>				1.704% = 1/58.68				
	Sediment	Pore Water (C_{free})	Aqueous Solubility	Narcosis FCV	Pore Water Toxic Units	PWRGs	PWRG Toxic Units	Site-Specific Log K_{OC}	Bulk Sediment PRWGs
PAH	µg/g (dw)	µg/L	µg/L	µg/L		µg/L		L/kg (OC)	µg/g (dw)
Naphthalene	3.33	2.89	30,995	193.5	0.015	0.049	0.0003	4.154	0.057
C1-Naphthalenes	1.07	2.13		81.69	0.026	0.036	0.0004	3.794	0.018
C2-Naphthalenes	2.57	26.8 J		30.24	0.886	0.457	0.0151	3.074	0.044
C3-Naphthalenes	1.94	35.5 J		11.10	3.198	0.605	0.0545	2.830	0.033
C4-Naphthalenes	1.01	18.5 J		4.048	4.570	0.315	0.0779	2.830	0.017
Benzo[e]pyrene	5.69	0.387	4.012	0.9008	0.430	0.007	0.0073	5.260	0.097
Indeno[1,2,3-cd]pyrene	6.39	0.12 J		0.2750	0.436	0.002	0.0074	5.819	0.109
Dibenz[a,h]anthracene	1.82	0.055 J	0.6012	0.2825	0.195	0.001	0.0033	5.612	0.031
Benzo[ghi]perylene	6.40	0.173 J	0.2600	0.4391	0.394	0.003	0.0067	5.661	0.109
Total Organic Carbon	8.08%								
Total	191.27	-	-	-	58.681	-	1.0	-	3.260

Mixtures: PWRG Methodology

8) Remedial Goal Development for Mixtures

- Beyond $K_{OC:SS}$ and $f_{OC:SS}$ development just discussed

- Composition of mixture will vary across the site
- If low variability
  - Selecting a single composition should be straight forwards
- If high variability
  - Will require some work to determine appropriate values
    - » Spatial patterns
    - » Site history and knowledge may allow parsing of the variability
    - » Distribution of the values
    - » Subdividing the site

Consistency of Sediment Toxicity Testing Results and PWRGs

Consistency of Sediment Toxicity Testing Results and PWRGs

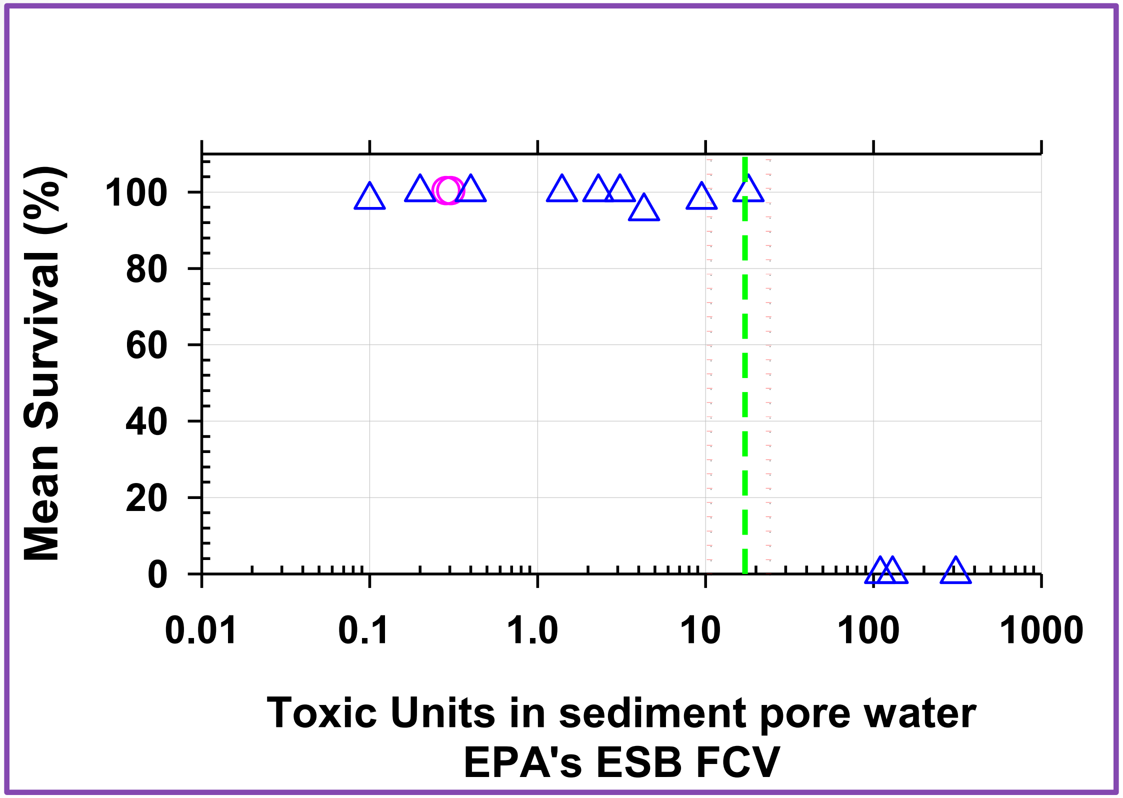
- Why?
  - In RI, sediment toxicity tests are often done
    - Benthic organisms
  - PWRG methodology for protection of benthic organisms

- When consistency exist
  - Reasonably assured the causes of toxicity are identified
  - Developed PWRGs will be protective of benthic organisms at the site

Toxicity Testing Results

PAH mixture species sensitivity distribution genus mean acute values for marine and freshwater toxicity testing species		
Species	Genus Mean Acute Value (µmole/ g octanol)	Percentage Rank of Genera
5th Percentile distribution value	FAV = 9.32	5.0%
Hyalella azteca**	13.9**	10.2%**
Leptocheirus plumulosus	19.0	22.4%
Rhepoxynius abronius	19.9	26.5%
Eohaustorius estuarius	22.1	32.6%
Ampelisca abdita	30.9	55.1%
Chironomus tentans	68.4	79.5%

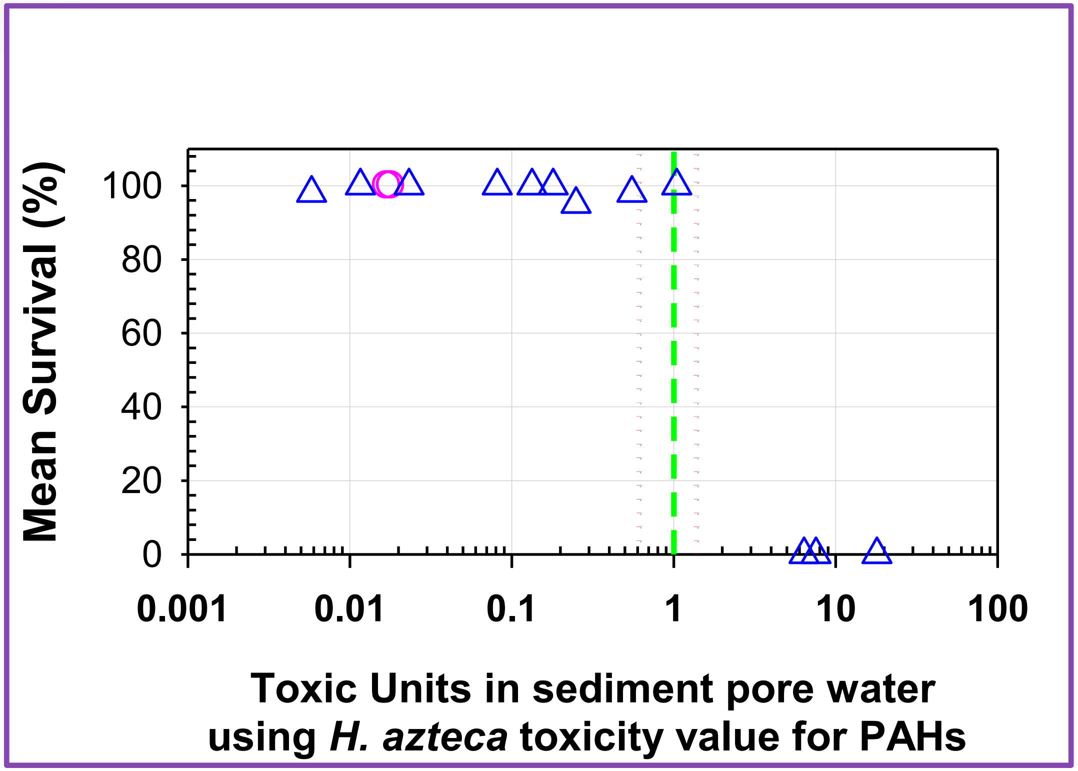
Toxicity Testing Results



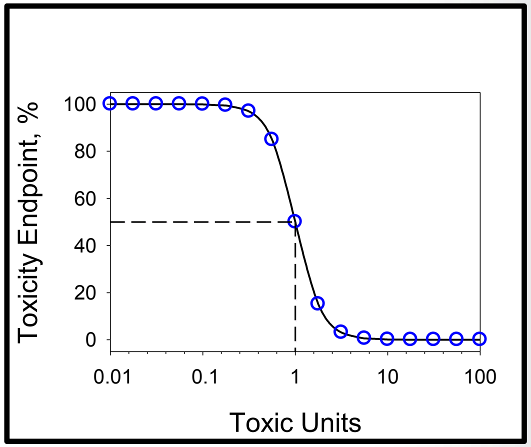
H. azteca less sensitive than the 5th percentile species for PAHs.

Measured sediment toxicity survival data for *Hyalella azteca* in 28-day test with sediments contaminated with PAHs (Kreitinger et al 2007). **- - - -** and •••• lines are the mean and 95% confidence levels for the EC50 derived from the water-only toxicity testing data for *H. azteca*.

Toxicity Testing Results

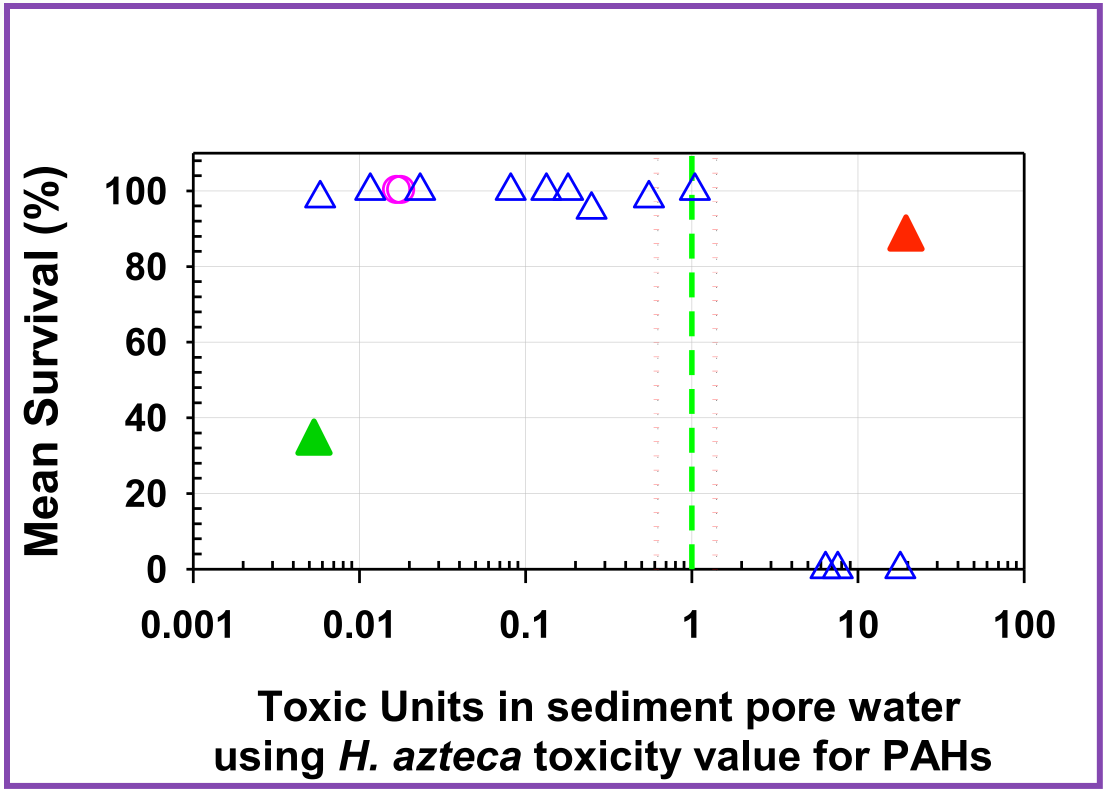


Results follow dose-response curve and breakpoint aligns with toxicity data for *H. azteca.*



Measured sediment toxicity survival data for *Hyalella azteca* in 28-day test with sediments contaminated with PAHs (Kreitinger et al 2007). **- - - -** and **••••** lines are the mean and 95% confidence levels for the EC50 derived from the water-only toxicity testing data for *H. azteca*.

Toxicity Testing Results



If data exists in the data set illustrated by

▲ - Suggests: Presence of other unidentified toxicants

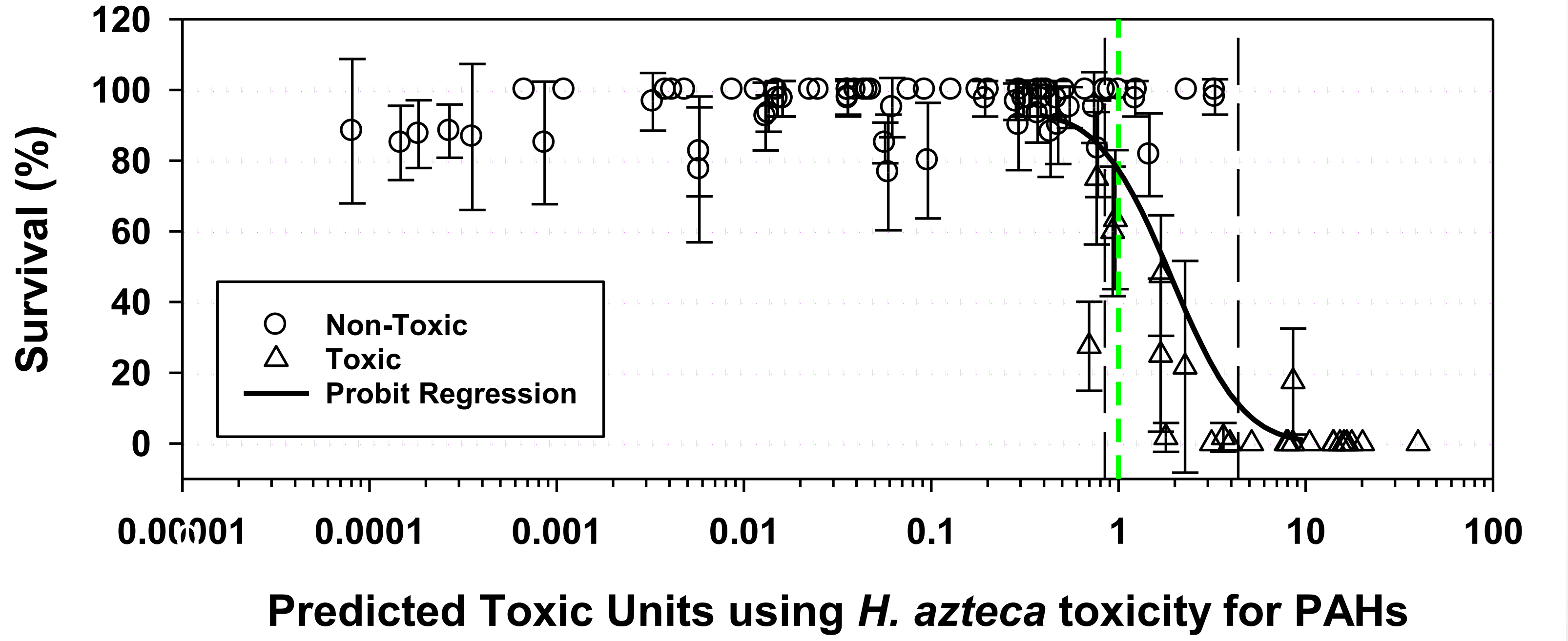
▲ - Suggests: Wrong toxicants have been identified

Consistency not demonstrated!

Measured sediment toxicity survival data for *Hyalella azteca* in 28-day test with sediments contaminated with PAHs (Kreitinger et al 2007). The - - - - and •••• lines are the mean and 95% confidence levels for the EC50 derived from the water-only toxicity testing data.

Toxicity Testing Results

- 28-day survival data for 97 samples from six MPG and two Al-smelter sites (Hawthorne et al. 2007)
  - Results:
    - Form dose-response shape
    - Breakpoint between toxic and non-toxic samples
    - Breakpoint centered around 1.0 TU



Summary

PWRG Methodology

- Methodology applicable to
  - Protection of benthic organisms from direct toxicity from sediment contaminants
  - Applicable to nonpolar organic chemicals
    - PAHs, chlorinated benzenes, pesticides …
- Methodology not applicable to
  - Effects resulting from bioaccumulation via the food chain
    - PCBs & PCDD/PCDFs
  - Higher trophic level benthic species
    - Crab, lobster, catfish, carp
  - Pelagic species
  - Cationic metals (Cu, Cd, Zn, Pb, Ni, Ag) & polar organics
    - Passive samplers in different stage of development

Summary

- Guidance available
  - EPA 600/R-15/289

- Looking for case study sites
  - Develop examples