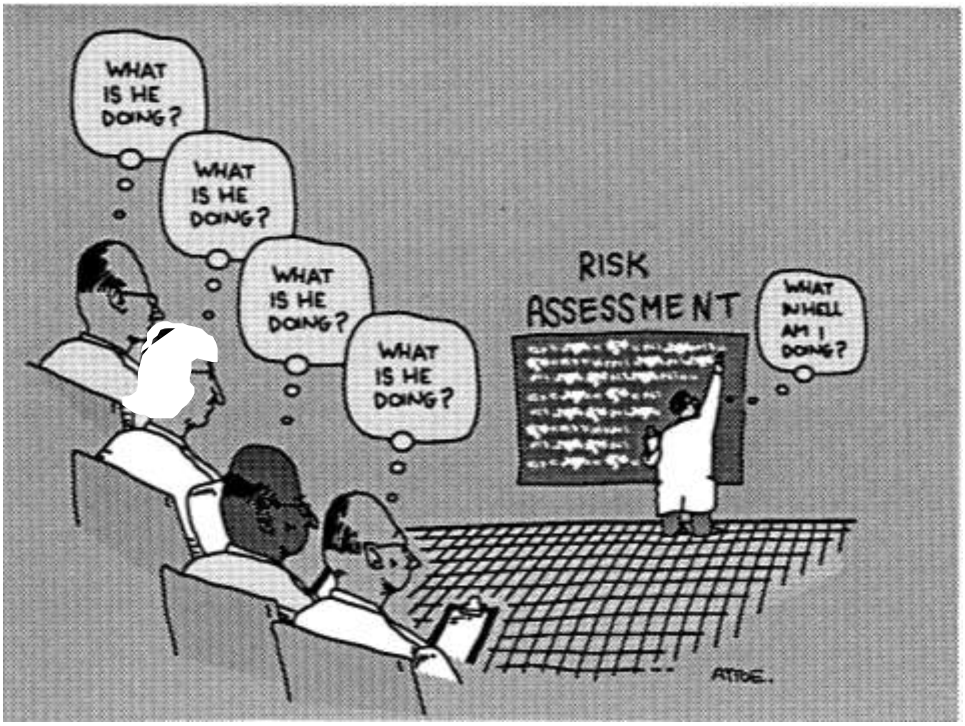

Advantages and Limitation of Using Various Sediment Quality Guidelines

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Blue slides from Mount and Berry (EPA)

Sources of Sediment Contaminants

- Existing and historical point sources discharges
  - Industrial discharge
  - Sewage treatment
- Atmospheric deposition of contaminants
  - Fuel combustion
  - Waste incineration
- Nonpoint source runoff
  - Harvested croplands (agricultural runoff)
  - Landfills, toxic waste storage and disposal sites
  - Urban stormwater
  - Inactive and abandoned mining sites

What standards and techniques exist to assess ecological risk of sediment contaminantion?

Two Families of Approaches

- Empirically-Derived approaches
  - Biological:chemical correlative
  - Can help to answer the question, "Would we predict this sediment to be toxic?"
- Equilibrium Partitioning (EqP) Approach
  - Theoretically derived from partitioning theory.
  - Can help answer the question, "Can this contaminant, at this concentration, in this sediment, contribute to toxicity?"

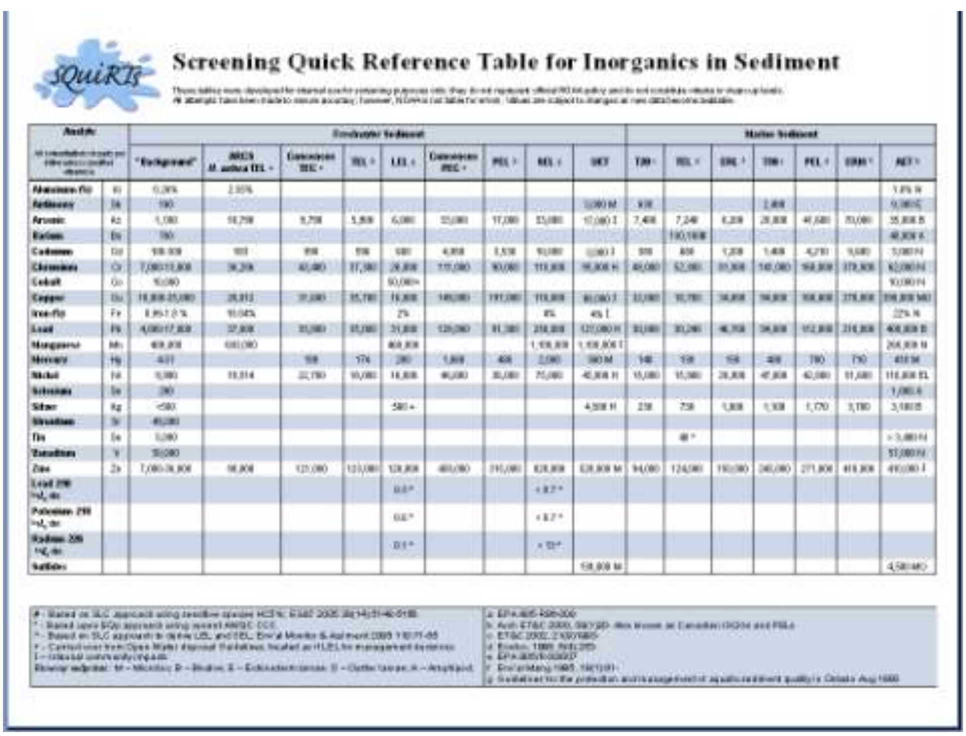
Selected Empirically-Derived Approaches

- Effects Approach:
  - ERL = Effects Range Low
  - ERM = Effects Range Median.
- Effects Level Approach:
  - TEL = Threshold Effects Level
  - PEL = Probable Effects Level
- Apparent Effects Threshold (AET)
- Logistic Regression Model Approach

SQGs of note

- Fresh water TEL/PEL
- Fresh water TEC/PEC
- Salt water ERL/ERM

- Got to the NOAA Screening Quick Reference Tables – Google: NOAA SQuiRT



Sediment Quality Guidelines

- Interpret historical data
- Source control
- Design monitoring programs
- Classify hot spots
- Identify potential problem chemicals or areas at a site
- Make decisions for more detailed study

But they do not provide cleanup concentrations

Nor were they ever designed to

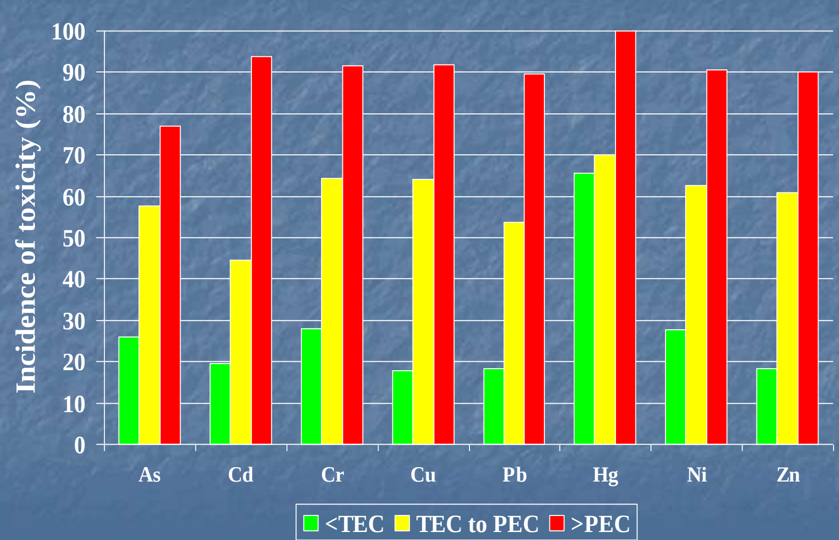
Development of consensus-based sediment quality guidelines (SQGs) for fresh water:

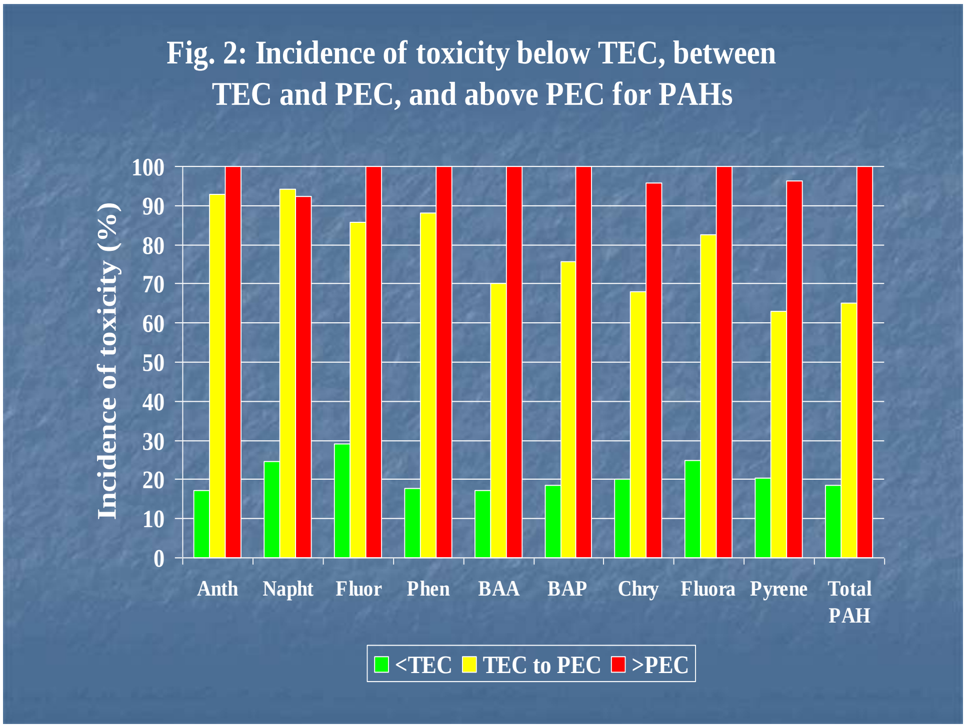
- Probable effect concentrations (PECs)
- Threshold effect concentrations (TECs)

Evaluate the predictive ability of SQGs:

- *Hyalella azteca*: 10- to 14-d tests (n=668)
- *Hyalella azteca*: 10- to 42-d tests (n=160)
- *Chironomus tentans*: 10- to 14-d tests (n=632)

Fig. 1: Incidence of toxicity below TEC, between TEC and PEC, and above PEC for metals





Is it ecologically worse to find several contaminants above the PEC or is it equally bad to find just one above the PEC? Does it make more sense to assess contaminants individually or as a composite in terms of ecological impacts?

Predictive Ability of SQGs:

Evaluate approaches for evaluating effects of chemical mixtures on toxicity in field-collected sediments.

- Mean PEC quotients:
  1. Divide concentration of chemical by PEC.
  2. Sum individual quotients.
  3. Calculate mean quotient/sample.

Evaluate ability of PECs to predict sediment toxicity in a freshwater database on a national and regional basis.

USGS

$$\text{ERM-Q} = \frac{1}{n}\sum_{i=1}^{n}\frac{COC_i}{ERM_i}$$

PEC Quotients

<0.1 = 18%

0.1 - <0.5 = 16%

0.5 – 1.0 = 37%

>1.0 = 54%

>5.0 = 71%

From: Ingersoll et al., 2001

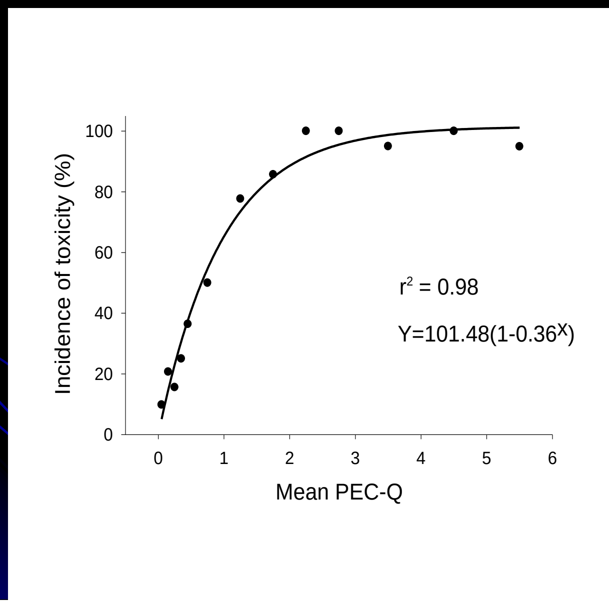
#of PELs / ER-Ms Exceeded

- 1 = 14%/23%
- 2 = 38%/37%
- 3 = 35%/24%
- 4 = 22%/63%

Percent = Highly Toxic

From: Long et al., 1998

Relationship between mean PEC-Q and the incidence of toxicity in freshwater sediments (n=347).



Are some contaminants worse than others ecologically? Or, if you are over the PEC, then you are equally bad? Is it worse if we find PCBs or chromium, for example?

Will the same concentration have different ecological effects based on geology or water chemistry or in different parts of a river?

PCBs: Often low toxicity in 10-day tox tests but bioaccumulates and biomagnifys. Some CBRs are available. SQGs are low.

PAHs: Toxic to benthic organisms but generally does not accumulate in finfish. Use histopathology or biomarkers

Metals: Toxic to benthic organisms but generally does not bioaccumulate or biomagnify in fish (except Hg and Cd)

Mercury: SQGs show low accuracy. MeHg is the more toxic form. Bioaccumulates and biomagnifies

Dioxin: Most difficult to address. No SQG, need TCDD Toxicity Reference Value after TEC (TEQ) calculation

But likely finer grained, higher TOC and AVS in impoundments

Develop Concentration-Response Relationships

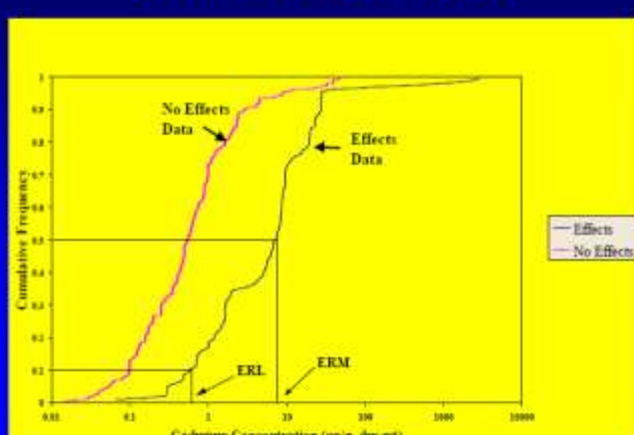
Approach:

- Compiled matching sediment chemistry and toxicity data
- Determined relationships between concentration and response for each COPC and COPC mixture for multiple species and endpoints (e.g., amphipod survival)

ERL and ERM derived

- Effects and no effects data from samples with concurrent biological effects and chemistry data are plotted with increasing concentration, against cumulative frequency.
- ERL is the tenth percentile of the effects data, ERM is the 50th percentile of the effects data.

Cumulative Frequency of Cadmium Concentration in BEDS Data Base: Derivation of ERL and ERM



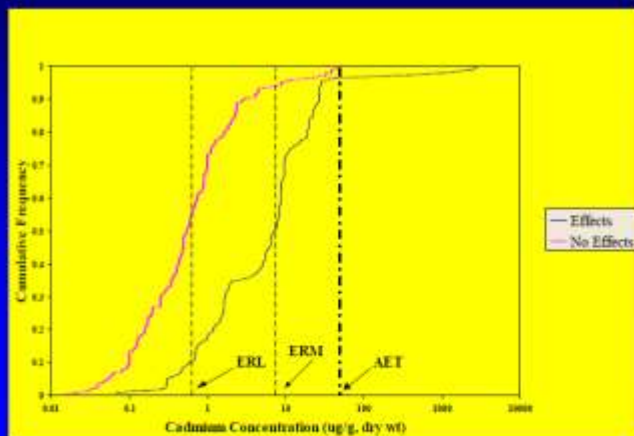
ERL and ERM Uses

- Most samples below the ERL are not toxic.
- Most of the samples above the ERM are toxic.
- Usually ERL and ERM values from multiple chemicals are used together, and/or quotients are calculated.
- Exceedance of a guideline does not mean that a particular chemical caused the toxicity.

AET Derivation

- The Apparent Effects Threshold (AET) is the concentration in the no-effects samples that has the highest concentration of a given contaminant.

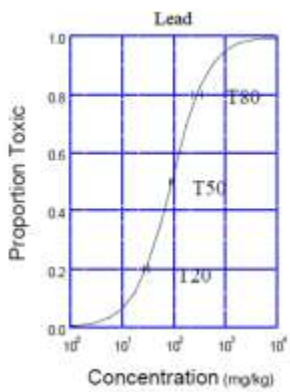
Cumulative Frequency of Cadmium Concentration in BEDS Data Base: Effect/Noeffect relative to AET



Logistic Regression Models (LRM) Approach

- LRM approach fits logistic regressions of proportion toxic samples in amphipod tests vs. concentration in a large field database.
- First, individual chemicals are fit.
- Then, combined models are fit using either the average probability of toxicity for all chemicals in a sample (p_AVG) or the maximum probability (p_MAX).

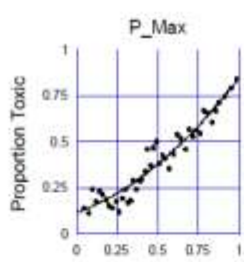
Individual Chemical Logistic Regression Models



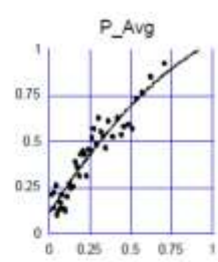
- Logistic model estimates the proportion of samples expected to be toxic at a given concentration
- Derived from screened data for marine amphipod survival
- Normalized chi-square statistic provides a relative measure of the goodness-of-fit for the individual chemical models
- Point estimates (e.g., T20, T50, T80) represent the concentration at which 20, 50, or 80% of the samples would be predicted to be toxic

After J. Field

Combined Models



$Y = 0.11+0.33x+0.40x^2$
$R^2 = 0.93$



$Y = 0.11+1.42x-0.48x^2$
$R^2 = 0.89$

After J. Field

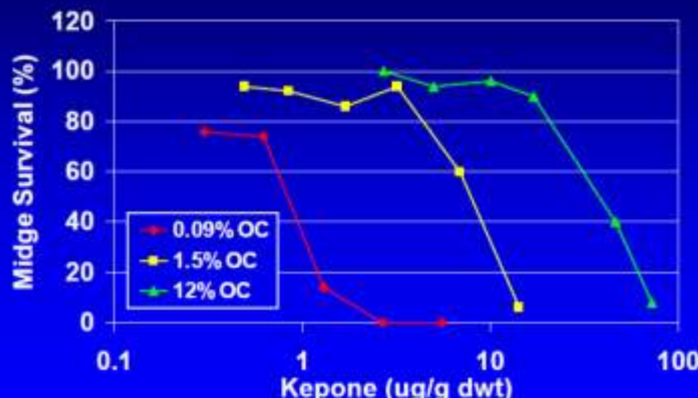
Shortcomings of Empirical SQGs

- Site-specific response dependent on composition of sediment and co-occurring contaminants
- Not causally-based; can't evaluate risk on a chemical-specific basis
- Don't provide a framework for developing remedial targets

Desirable Traits for SQGs

- Linked to risk from specific chemicals
- Coherent with underlying toxicology
- Causal basis
- Addresses effects of sediment matrix on bioavailability of contaminants

Toxicity of Kepone Different in Different Sediments



Adams et al. (1985)

Two Families of Approaches

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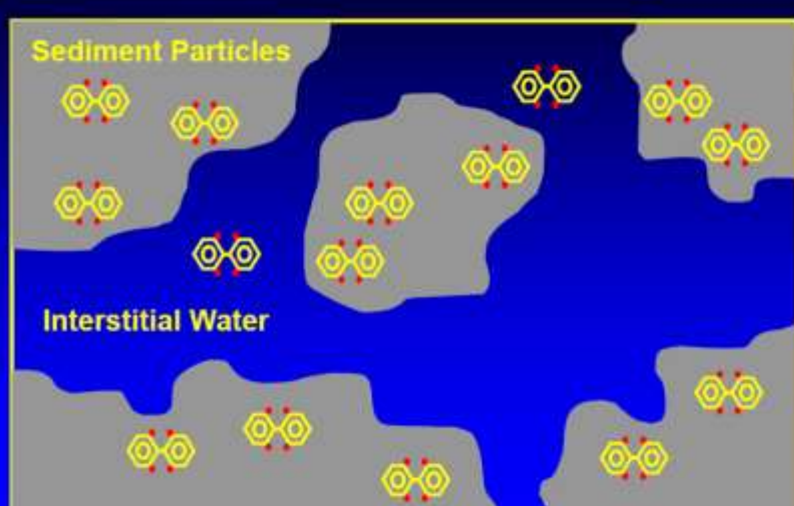
Organic Carbon Partition Coefficient (K_{OC})

$$K_{OC} = \frac{C_{organic\ carbon}}{C_{water}}$$

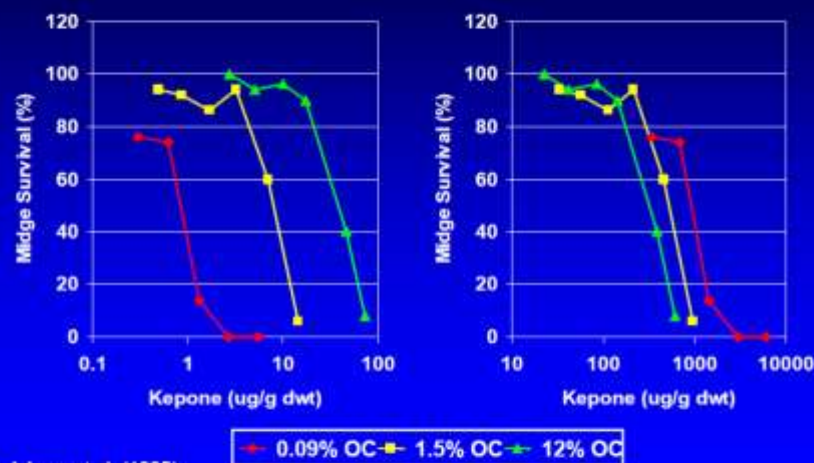
$$K_{OC} = \frac{3000\ ug/kg}{3\ ug/L} = 1000\ L/kg$$

$$\text{Log } K_{OC} \approx \text{Log } K_{OW}$$

PCB Distribution in Sediment

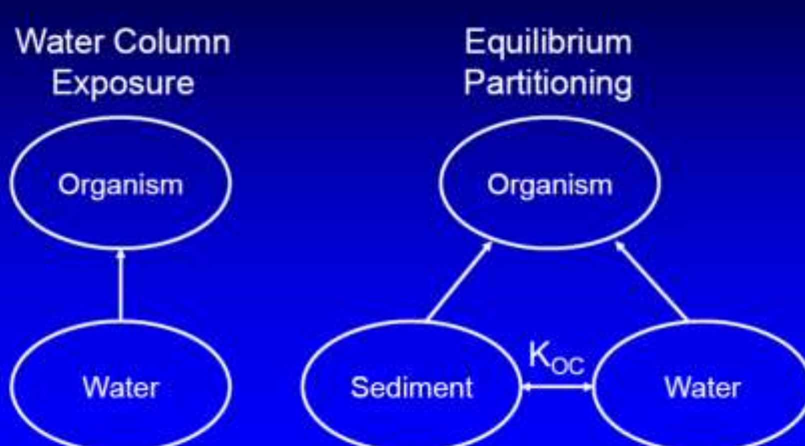


Organic Carbon Normalization Reduces Variability Among Sediments



Adams et al. (1985)

Equilibrium Partitioning (EqP)



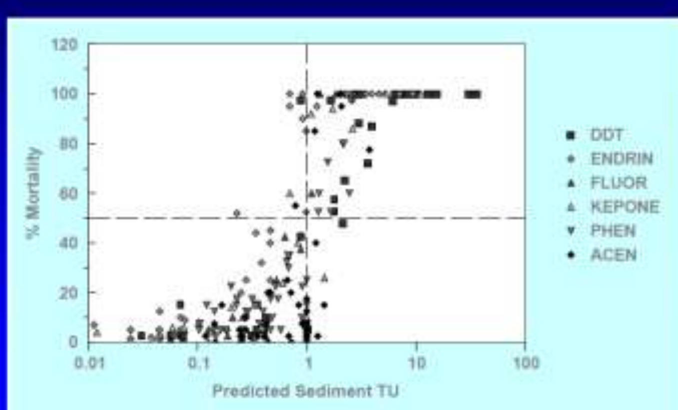
How Do I Calculate an SQG Using EQP?

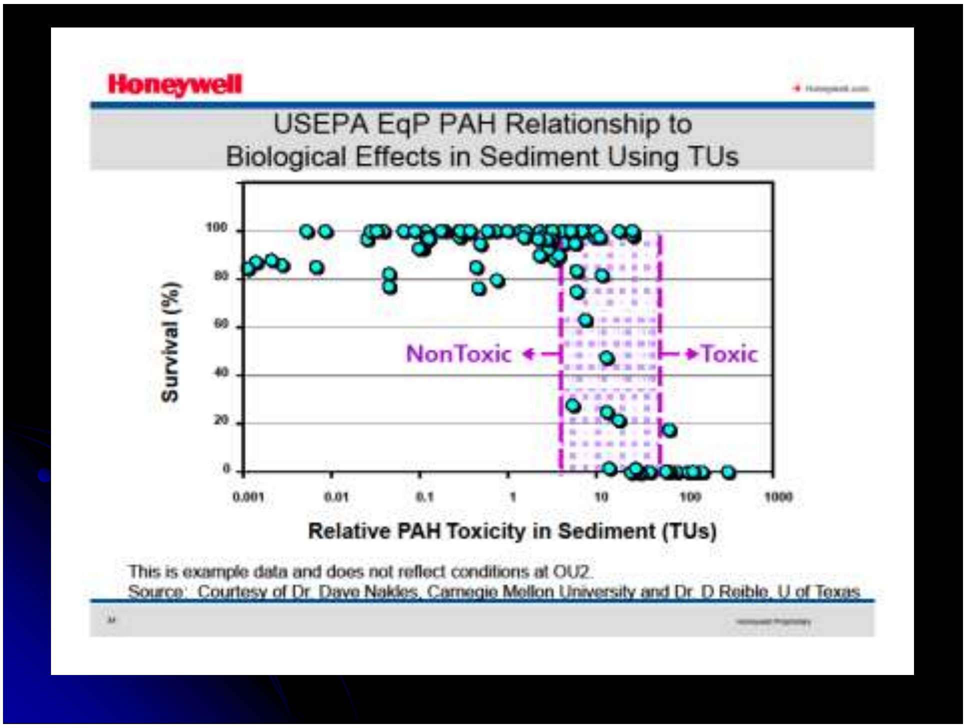
Choose a water column effect benchmark: C_{water} = AWQC

We know that: $K_{OC} = C_{organic\ carbon} / C_{water}$

So: $C_{SQG\ (oc)} = K_{OC} * C_{water}$ = KOC*AWQC

EqP Predicts Toxicity for Many Chemicals, Organisms, Sediments





What if I'm Interested in Another Endpoint?

Example: DDT — log K_{OC} = 6.42

Hyalella LC50 = 0.45 ug/L

$$C_{effect(oc)} = K_{OC} * C_{water}$$
$$= 10^{6.42} \text{ L/kg OC} * 0.45 \text{ ug/L}$$
$$= 1180000 \text{ ug/kg OC}$$
$$= 1180 \text{ ug/g OC}$$

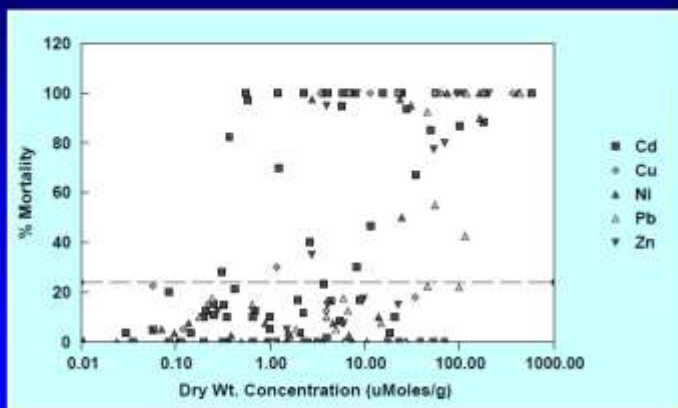
What About Metals?

- Same general principle applies to metals
- Partitioning of Cu, Cd, Pb, Zn, Ni, Ag in anoxic sediments dominated by binding to sulfides
- Binding capacity measured as "acid volatile sulfide" (AVS)
- Metals measured as "simultaneously extracted metals" (SEM)
- If more metal than sulfide (SEM-AVS>0) then potential for metal toxicity

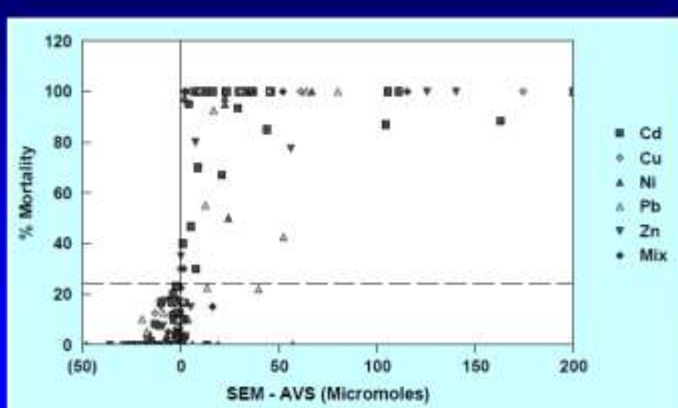
AVS

In the aquatic environment, the bioavailability of metals is generally controlled by different water and sediment variables. Sediment characteristics such as organic matter, iron and manganese oxides, carbonates, and clay content can bind metal ions and therefore reduce their availability to aquatic organisms*. In anaerobic sediments, sulfate* reduction by anoxic bacteria leads to the formation of sulfides, which are called acid volatile sulfides (AVS). AVS is operationally defined as the amount of sulfides volatilized by the addition of 1 N HCl and consists mainly of iron- and manganese sulfides*. In their reaction with metals, AVS* form thermodynamically stable metal sulfide precipitates, which results in a decreased concentration of free metal ions and therefore reduced metal bioavailability in the sediment pore water*.*

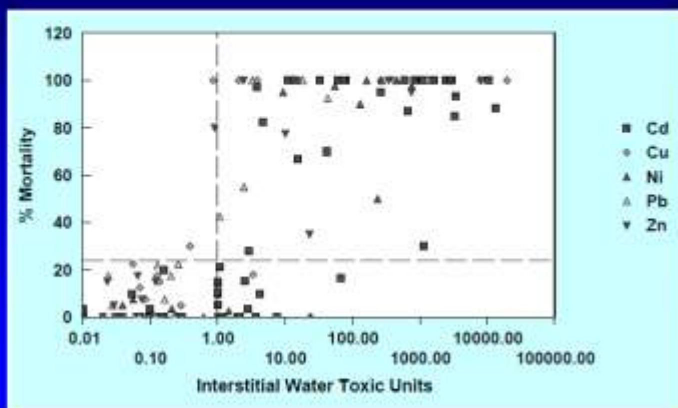
Toxicity of Metals on Dry Weight Basis Varies Widely



Toxicity Observed Only When SEM Metal Exceeds AVS



No Toxicity When Metals Are Low in Interstitial Water



EqP -- Not Just for Breakfast Anymore

- EqP can be used to generate sediment quality guidelines
- Yes, but. . .its greater importance might be as a framework for understanding sediment contamination and associated risks, not just for screening values

Conclusions: Using Both Empirical and EqP Guidelines

- Nickel ERL and ERM seem to "work": all stations with nickel < ERL were not toxic, all stations with nickel > ERM were toxic.
- AVS guideline did not predict toxicity at these stations: many stations with SEM-AVS <0 were toxic. All stations with SEM-AVS >0 were not toxic.
- No metal present in the IW at any stations.
- Conclusion: toxicity is not due to metals.

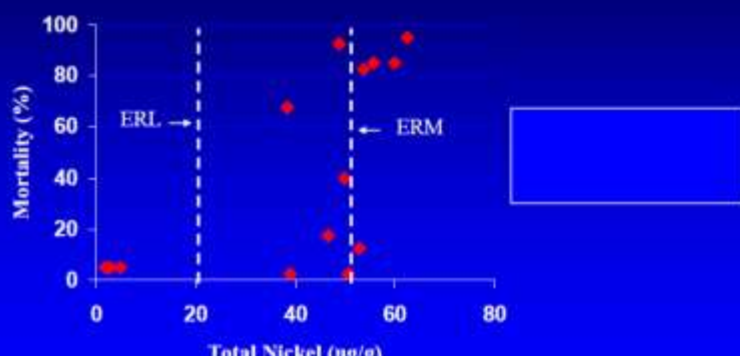
Using both Empirical and EqP Guidelines: Moral to the Story

- Just because an empirical guideline is exceeded, does not mean that particular chemical is causing the toxicity.
- EqP guidelines may not predict toxicity in mixed chemical situations (the guidelines only work for the chemicals that you have guidelines for)
- Chemistry guidelines are only one tool in the toolbox.

Which guideline should I use?

- What if different guidelines give different "answers"?

Mortality vs. Nickel from a site where metals are not causing the toxicity: Compared to ERL and ERM for Nickel



Background or Reference

An average or expected amount of a substance in a specific environment.

Difficult to establish an acceptable background or reference sediment

Less contamination

Similar physical characteristics

Removal costs

Landfill costs based on “leaching test” (Toxicity Characteristic Leaching Procedure or TCLP)

Used to determine if soil/sediment can enter a municipal landfill (RCRA D) or a hazardous waste landfill (RCRA C).

The TCLP test does not measure concentration; rather, it measures the potential for contaminants to seep or "leach" into groundwater if a waste is landfill disposed.

The test could cost as high as $3000

Chemistry costs

- Metals: $180
- SVOC: $320 to $520
- PCBs: $160
- Pesticides: $180
- Conventional Parameters: $200

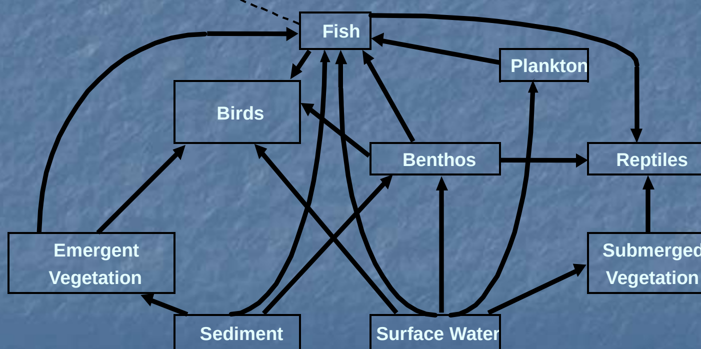
If there are more than five samples costs generally start to decrease per sample.

Toxicity Testing Costs

- 10-day Hyalella test: $1000 for survival endpoint only, $1100 for both survival and growth endpoints
- 10-day Chironomus test: $1000 for survival endpoint only, $1100 for both survival and growth endpoints

If there are more than five samples costs generally start to decrease per sample.

Simplified Foodweb



QUESTIONS