



Application of Passive Sampling and Environmental Quality Standards in Sediment Assessments in the United States

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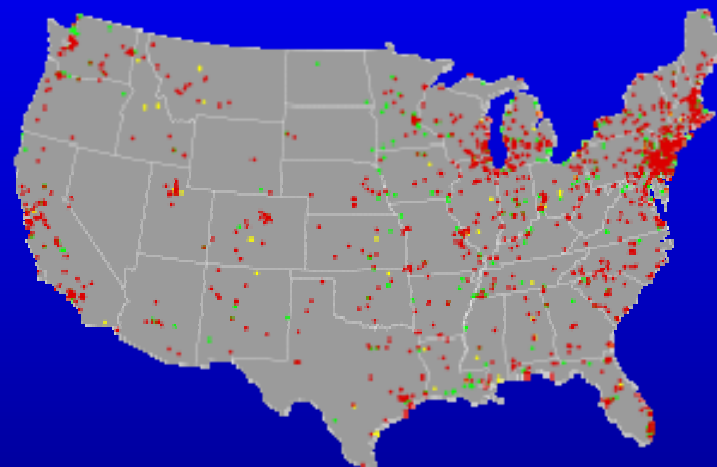
Background

- Contaminated sediments recognized as a serious source of risk in United States
 - National Research Council (2001, 2003) report 70% coastal ecosystems negatively affected (e.g., 2,800 fish advisories (i.e., fish unsafe to consume))
- Risk “Drivers”
 - Human health (i.e., cancer and non-cancer effects)
 - Ecological effects (i.e., toxicity, bioaccumulation)
 - Need to perform sediment assessments to properly assess ecological risk
- Superfund Program
 - Empowers U.S. EPA to clean-up contaminated sites and compel responsible parties to perform cleanups or reimburse the government for EPA-lead cleanups



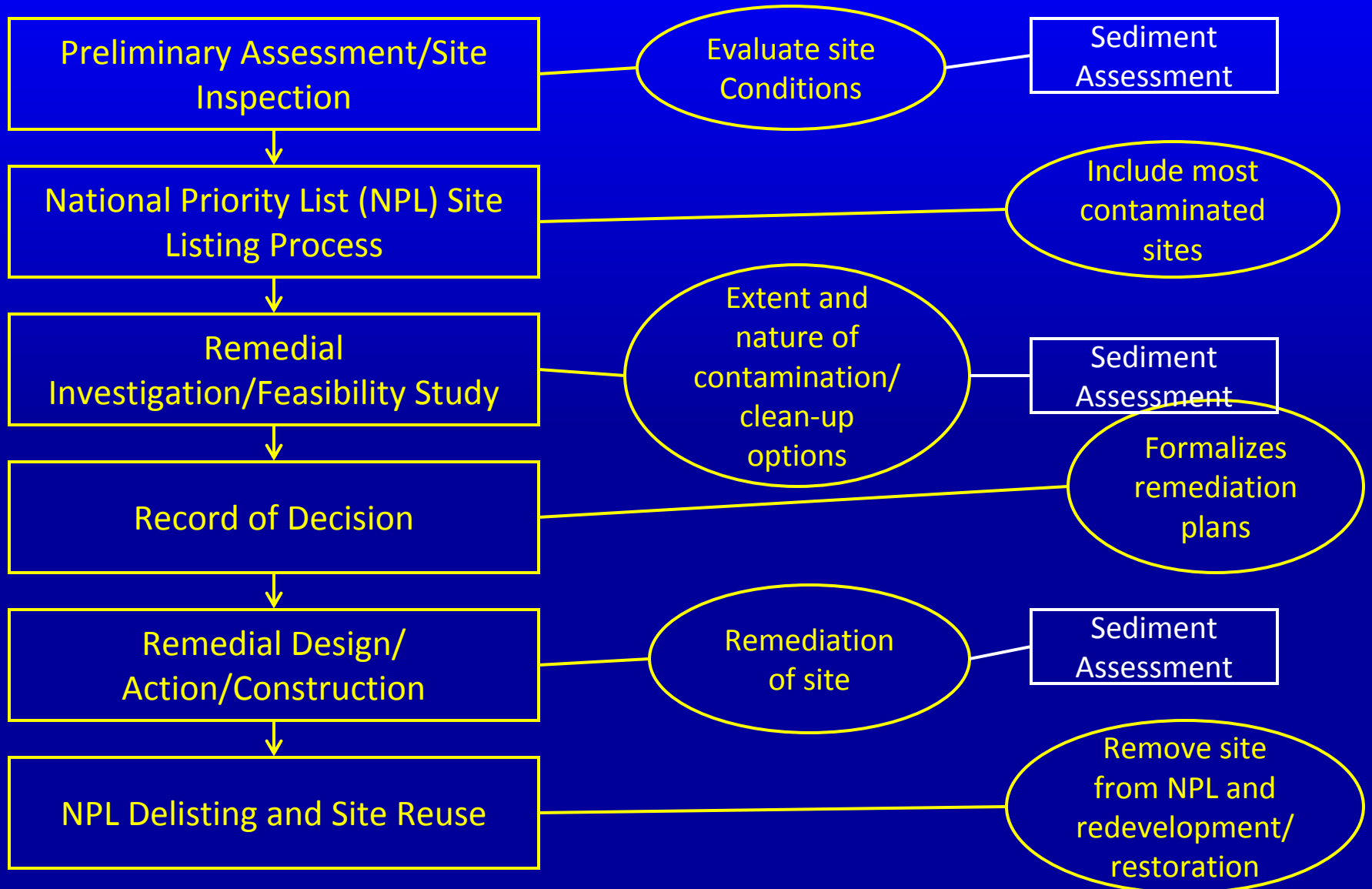
Superfund Program

- 40,000 sites around the United States investigated
- As of 2010, 1080 most hazardous sites remediated
- Focus on “Priority Pollutants” (n = 126)
 - PCBs, PAHs, arsenic, cadmium, lead, mercury, volatile organics



Map of Superfund sites in the contiguous United States. Red indicates currently active sites, yellow are proposed, green have been deleted (usually meaning having been cleaned up) (March 2010).

Superfund Program



Sediment Assessment

Superfund Program Goal:

Increase information
robustness while
controlling costs

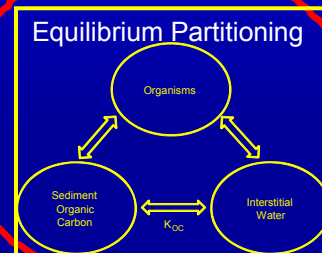
Cost (€ or Kč or \$)



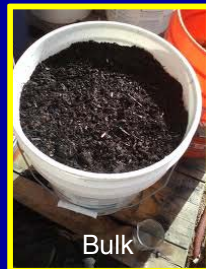
Measure of
contaminant
bioavailability and
adverse effects



Measure of
contaminant bioavailability

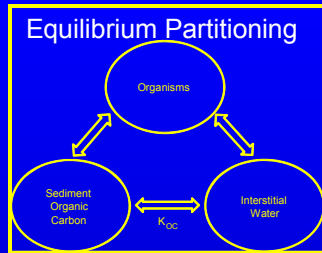


Estimate of
contaminant bioavailability



Gross measure of
contaminant presence

Information Robustness



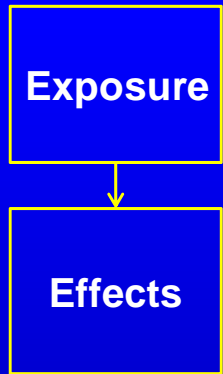
Equilibrium Partitioning

- Applied to derive mechanistic Sediment Quality Guidelines (SQGs)
 - Equilibrium Partitioning Sediment Benchmarks (ESBs)
 - Endrin
 - Dieldrin
 - Polycyclic Aromatic Hydrocarbon (PAH) Mixtures
 - Compendium of 32 Organic Compounds
 - An ether; Low molecular weight; Pesticides; Phthalates
 - Metal Mixtures (Ag, Cd, Cu, Ni, Pb, Zn) & Cr
 - $\Sigma = 73$ contaminants
 - Di Toro et al. (1991) and Burgess et al. (2013)



Equilibrium Partitioning

- Conceptual Model: Exposure and effects
 - **Exposure** is based on Equilibrium Partitioning estimate of interstitial water concentrations (C_{ITW}) based on organic carbon (and black carbon) sorption
 - **Effects** are water-only U.S. EPA Ambient Water Quality Criteria (AWQC), a type of *Environmental Quality Standards (EQSs)*
 - Mathematically relate organic carbon normalized sediment concentration to water-only AWQC for a given contaminants (x)



$$ESB_x = K_{OCx} * AWQC_x$$

where, ESB is the Equilibrium Partitioning Sediment Benchmark ($\mu\text{g}/\text{Kg}_{OC}$) for Contaminant x and K_{OCx} is the organic carbon normalized partition coefficient (L/Kg_{OC}) for Contaminant x; AWQC in $\mu\text{g}/\text{L}$

EQS: Ambient Water Quality Criteria

- U.S. EPA develops and publishes criteria reflecting the latest scientific knowledge to protect aquatic life and designated uses

- Chemical-specific
- Numeric and narrative
- Saltwater and freshwater values
- Priority pollutants (organics, metals)



- Two regulatory values

- Criterion Maximum Concentration (CMC) = Short-term effects (acceptable one-hour mean concentration)
- Criterion Continuous Concentration (CCC) = Long-term effects (acceptable four-day mean concentration)

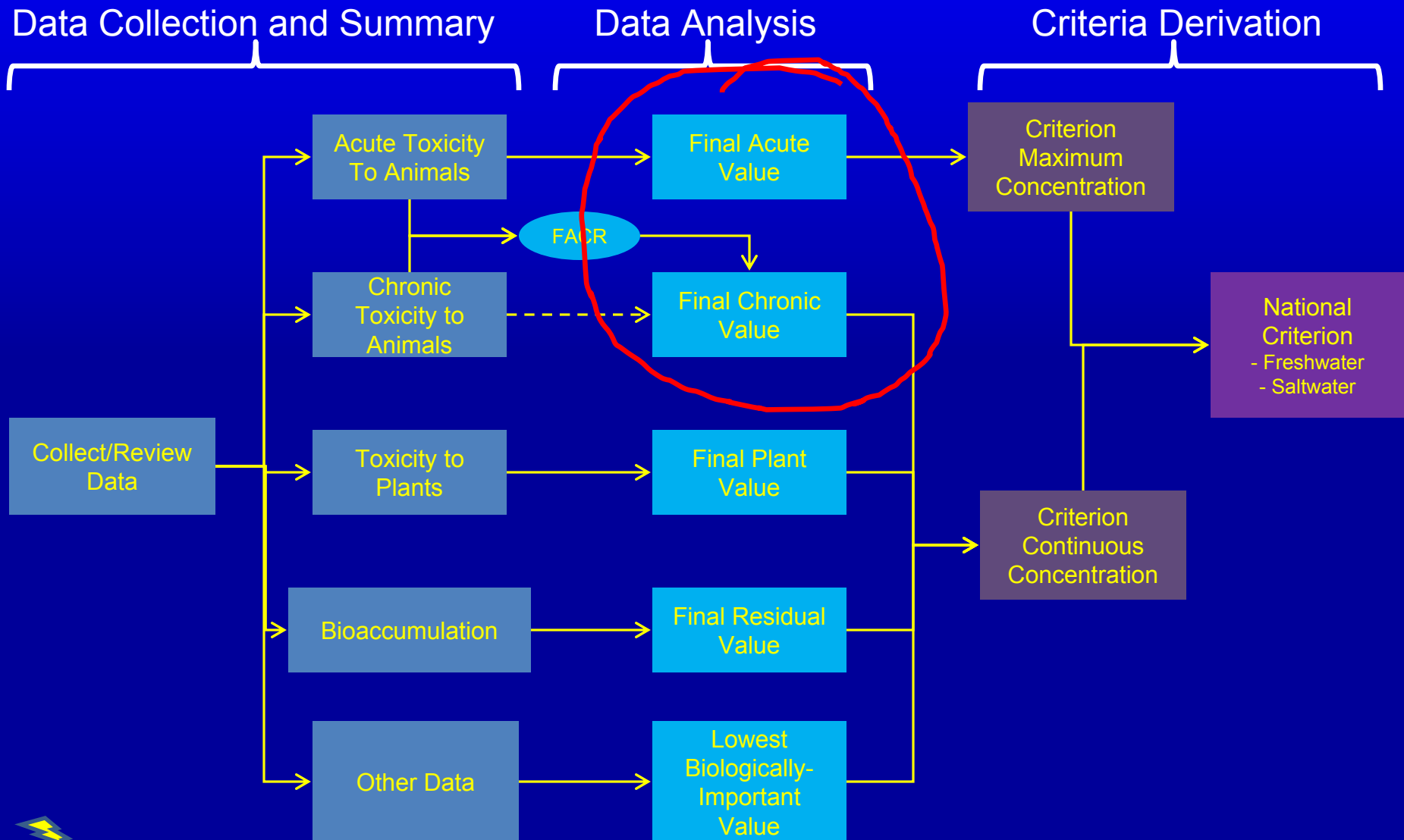
- Provide basis for controlling discharges or releases of pollutants

- *If this concentration is exceeded toxic effects to aquatic life will occur*



EQS: Ambient Water Quality Criteria

Derivation of Ambient Water Quality Criteria



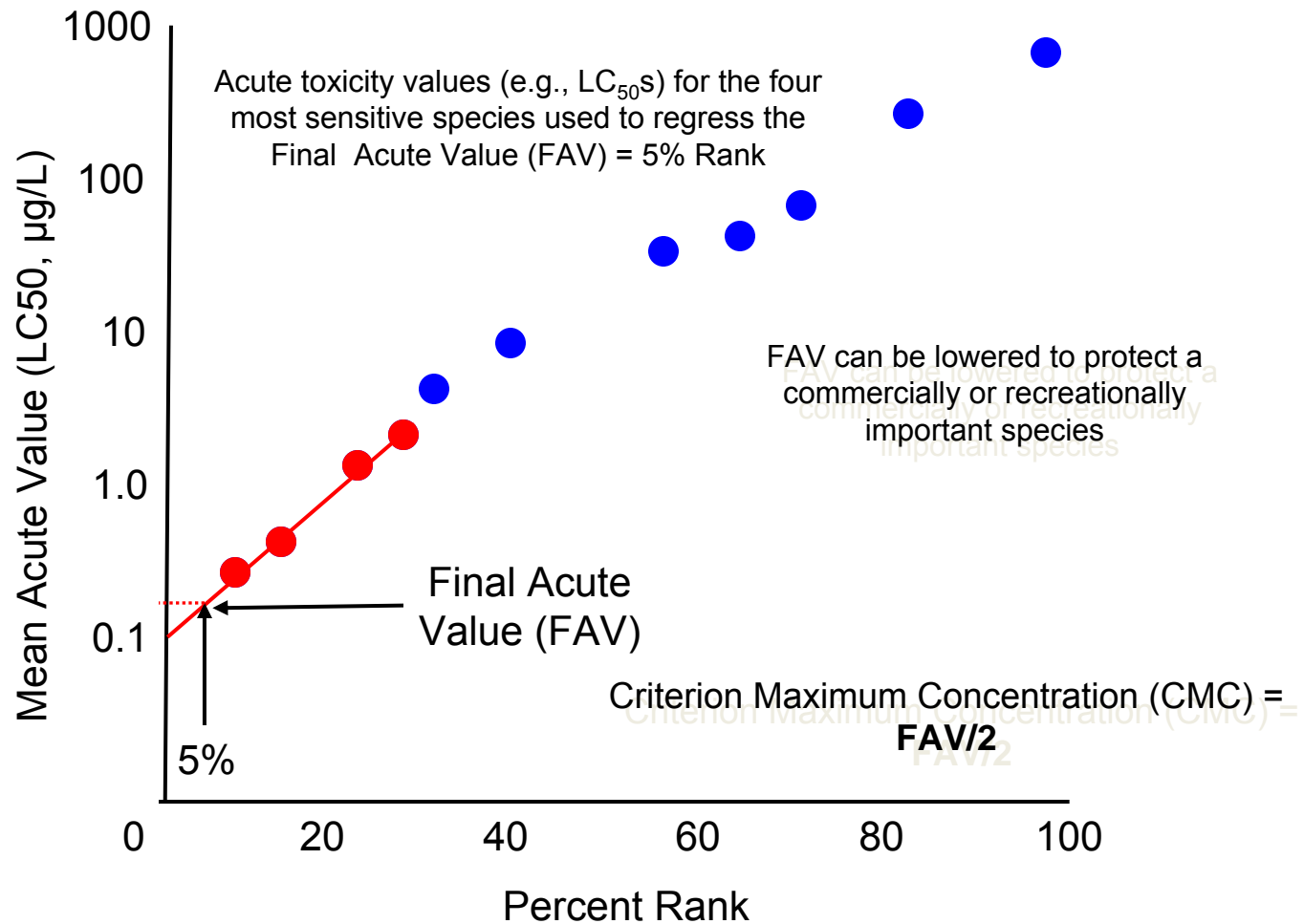
EQS: Ambient Water Quality Criteria

- Derivation of Ambient Water Quality Criteria (AWQC)
 - Approach described in Stephan et al. (1985): *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*
 - U.S. EPA Office of Water manages development of AWQC
 - Primarily two types of aquatic toxicity data: Acute and Chronic
 - Minimum dataset requirements (MDR)
 - Acute Data
 - Usually % survival of most sensitive life stage (e.g., 48 and 96 hour LC₅₀s)
 - 8 freshwater genera & 8 saltwater genera
 - Data spread across various families of fish and invertebrates representing the distribution of sensitivities within the aquatic community

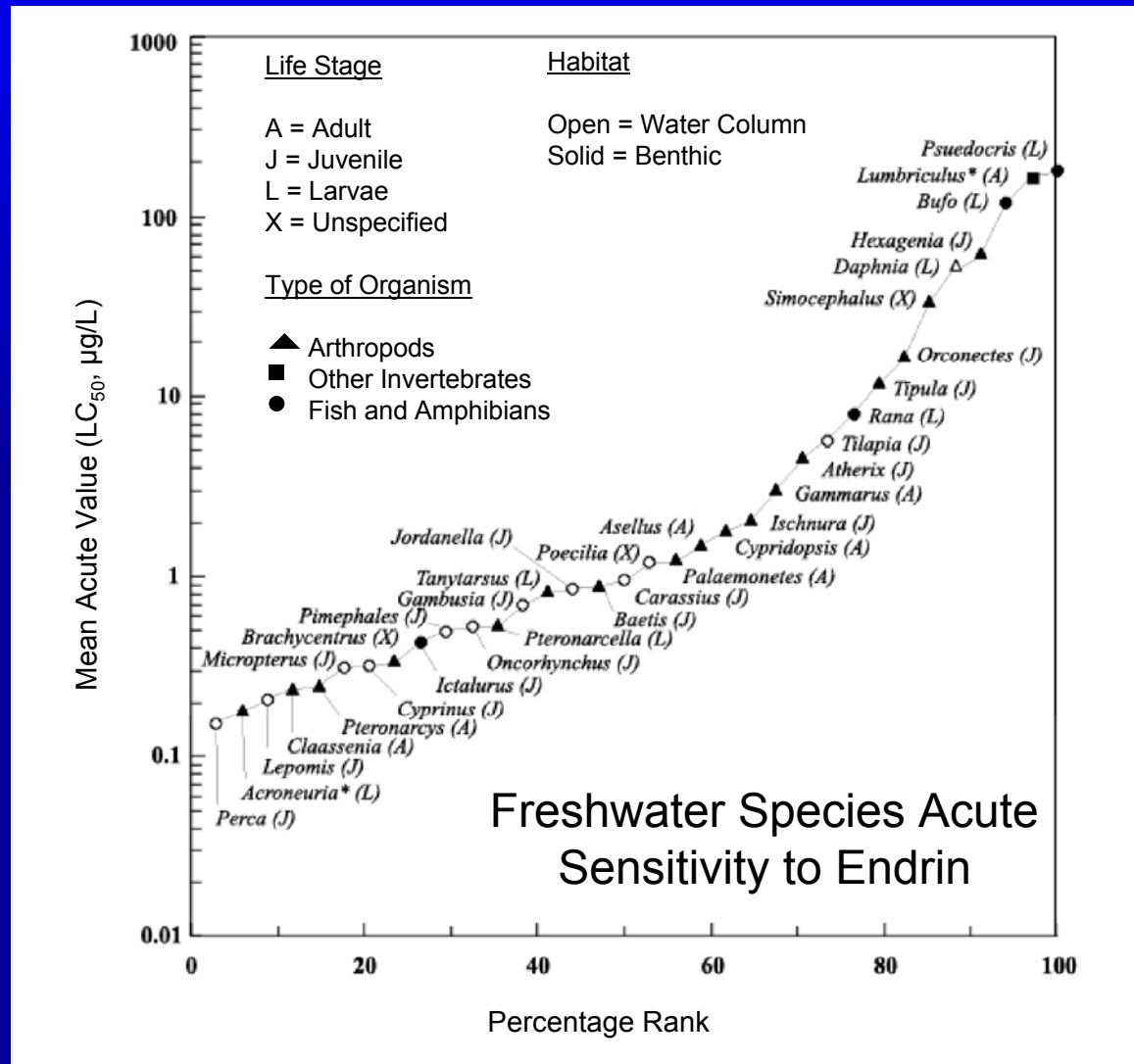
EQS: Ambient Water Quality Criteria

- Derivation of Ambient Water Quality Criteria (Cont.)
 - Chronic Data
 - Survival, growth and/or reproduction (e.g., 28 day chronic toxicity test)
 - Chronic No Effect Concentration (NOEC)
 - Geometric mean of NOEC and Lowest Effect Concentration (LOEC)
 - Chronic effect point estimate (e.g., EC₁₀)
 - One fish, one invertebrate and one acutely sensitive species
 - Frequently mixture of freshwater & saltwater species
 - Chemistry and Exposure Data
 - Measured concentrations preferred to unmeasured
 - Flow-through preferred to static or static-renewal exposures

Derivation of Criterion Maximum Concentration



EQS: Ambient Water Quality Criteria



EQS: Ambient Water Quality Criteria

- Derivation of Ambient Water Quality Criteria (cont.)
 - Final Chronic Value (FCV)
 - » Ideally, have sufficient chronic data to “regress” value (like FAV)
 - » $FCV = FAV / \text{Final Acute Chronic Ratio (FACR)}$
 - » FACR developed from available acute & chronic data
 - Criterion Continuous Concentration (CCC) equivalent to...
 - » FCV, Final Plant Value or “other data”
 - » Most frequently, the CCC is equivalent to the FCV
 - Site-specific criteria can be derived

EQS: Ambient Water Quality Criteria

Pollutant	CAS Number	Priority/ Non-Priority Pollutant	Freshwater		Saltwater		Publication Year
			CMC (µg/L)	CCC (µg/L)	CMC (µg/L)	CCC (µg/L)	
Acrolein	107028	P	3µg/L	3µg/L	-	-	2009
Aesthetic Qualities	—	NP	NARRATIVE STATEMENT—SEE DOCUMENT				1986
Aldrin	309002	P	3.0 ^G	-	1.3 ^G	-	1980
Alkalinity	—	NP	-	20000 ^C	-	-	1986
alpha-Endosulfan	959988	P	0.22 ^{G,Y}	0.056 ^{G,Y}	0.034 ^{G,Y}	0.0087 ^{G,Y}	1980
Aluminum (pH 6.5 – 9.0)	7429905	NP	750 ^I	87 ^{IS}	-	-	1988
Ammonia	7664417	NP	FRESHWATER CRITERIA ARE pH, Temperature and Life-stage DEPENDENT SALTWATER CRITERIA ARE pH AND Temperature DEPENDENT				1999
Arsenic	7440382	P	340 ^{A,D}	150 ^{A,D}	69 ^{A,D}	36 ^{A,D}	1995
Bacteria	—	NP	FOR PRIMARY RECREATION AND SHELLFISH USES—SEE DOCUMENT				1986
beta-Endosulfan	33213659	P	0.22 ^{G,Y}	0.056 ^{G,Y}	0.034 ^{G,Y}	0.0087 ^{G,Y}	1980
Boron	—	NP	NARRATIVE STATEMENT—SEE DOCUMENT				1986
Carbaryl	63252	NP	2.1	2.1	1.6	-	2012
Cadmium	7440439	P	2.0 ^{D,E}	0.25 ^{D,E}	40 ^D	8.8 ^D	2001

Documents/values available on-line (<http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm>)



EQS: Canadian Approach

- Derivation of Water Quality Guidelines
 - Approach described in *A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life 2007*
 - Authorized by Canadian Council of Ministers of the Environment (CCME)
 - Minimum dataset requirements determine type of guideline
 - Type A
 - Derived using species sensitivity distribution (SSD) fitted with primary and secondary toxicity data
 - Type B
 - Insufficient data for SSD but minimum number of primary and secondary toxicity data
 - Guideline values
 - Short-term (intermittent exposure (e.g., a spill))
 - Long-term (indefinite exposure)

EQS: Canadian Approach

- Derivation of Water Quality Guidelines (Cont.)
 - Consider environmental behavior, fate and persistence data
 - Exposure and route of uptake; Mode of toxic action; Bioavailability; Bioaccumulation
 - Toxicological Data
 - Data Quality
 - Primary Data: Scientifically defensible using currently acceptable laboratory and field practices
 - Secondary Data: Acceptable but not primary data
 - Short-term exposure
 - 96-hour LC50s
 - Long-term exposure
 - Point estimates (EC₁₀s) preferred to hypothesis-based endpoints (e.g., LOECs, NOECs)

EQS: Canadian Approach

- Derivation of Water Quality Guidelines (Cont.)
 - Both short- and long-term Type A guidelines
 - Species Sensitivity Distribution (SSD) is fit
 - No specific model is recommended
 - Guidelines lists several
 - 5% percentile defines the guideline value
 - For long-term guidelines, a “protection clause” can be invoked to lower the value
 - Site-specific guidelines are also viable

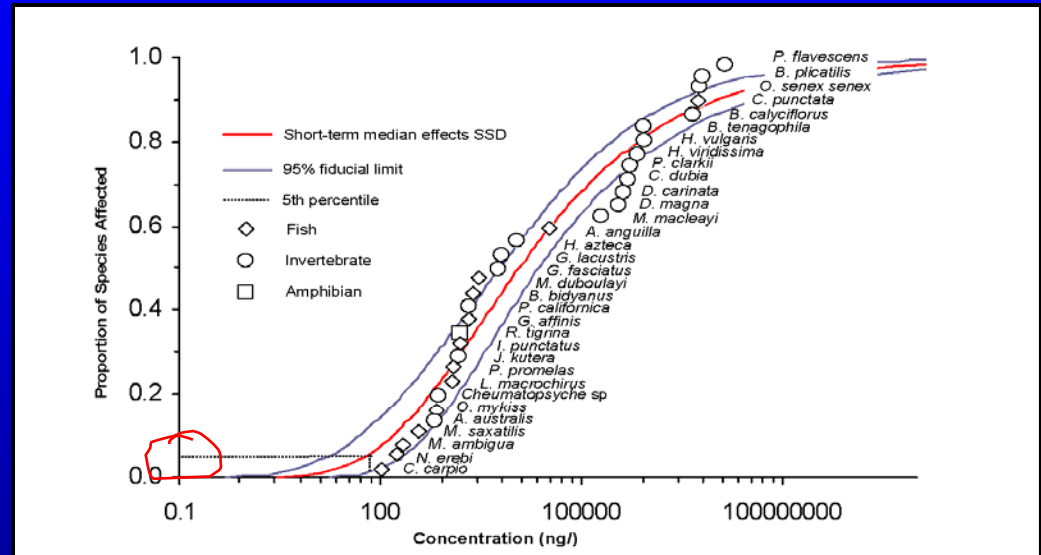


Figure 1. Short-term SSD representing the toxicity of endosulfan in freshwater consisting of acceptable short-term LC₅₀s of 33 aquatic species versus proportion of species affected.

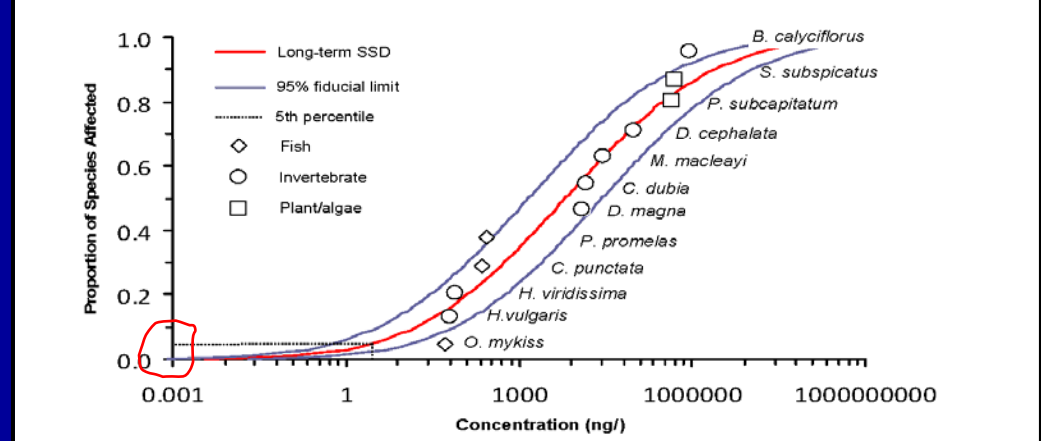
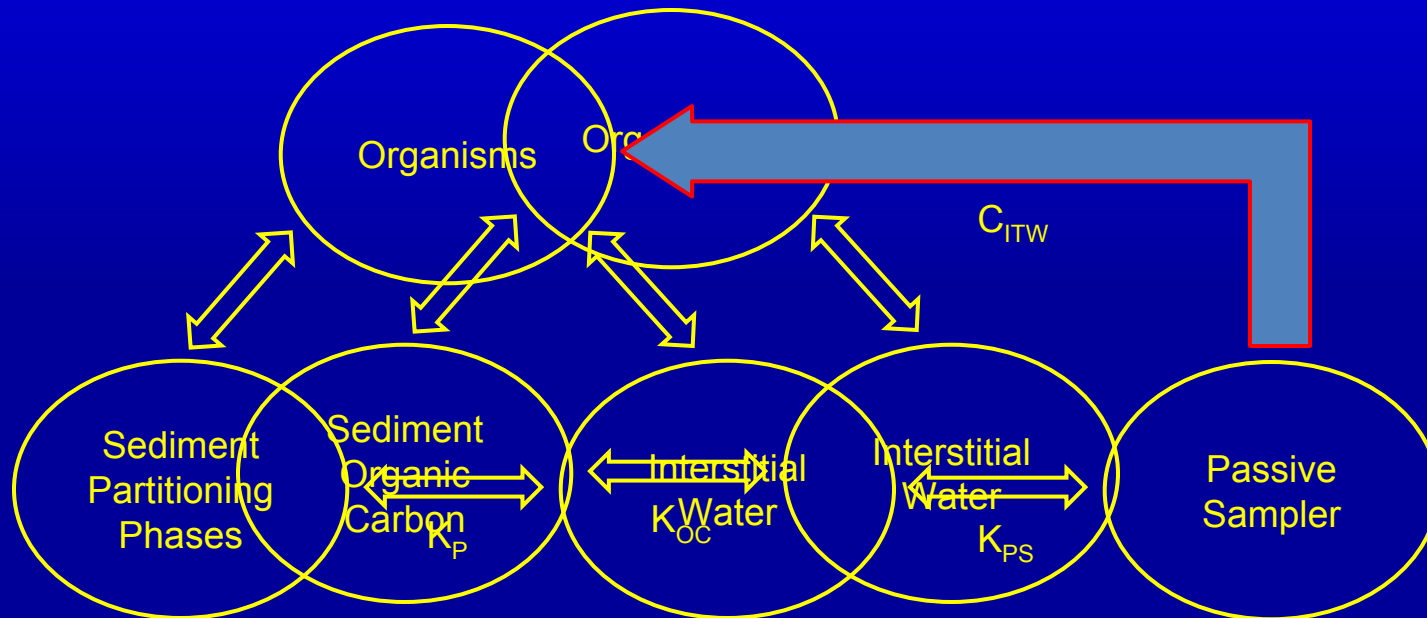


Figure 2. Long-term SSD representing the toxicity of endosulfan in freshwater consisting of acceptable long-term data endpoints of 12 aquatic species versus proportion of species affected.

Passive Sampling and EQS

Current Equilibrium Partitioning Model



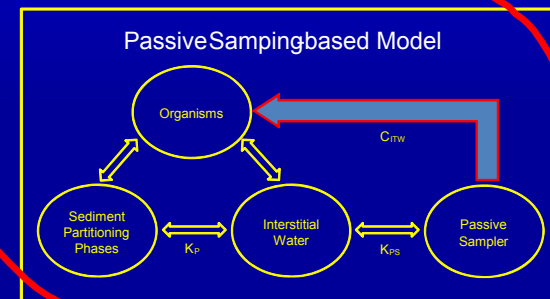
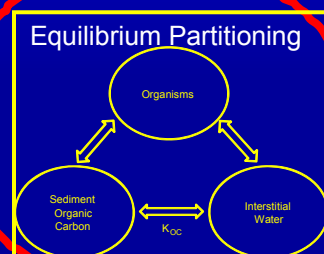
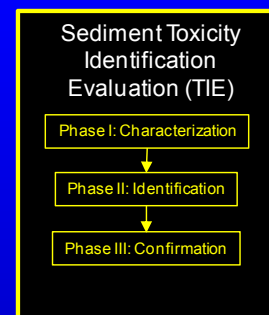
Compare equilibrium partitioning based estimate of interstitial water concentration to AWQC value



Sediment Assessment

Superfund Program Goal:
Increase information
robustness while
controlling costs

Cost (€ or Kč or \$)



Information Robustness

Summary

- Sediment assessment is a critical component of evaluating risk at contaminated sediment sites
 - Risk assessment approach
- Ambient Water Quality Criteria (i.e., EQSs) basis of the effects components
- Passive sampling offers cutting-edge scientifically-robust and cost-effective alternative to modeling sediment interstitial water concentrations (exposure)
- Focus here on Superfund Program, priority pollutants and contaminated sediments
 - Emerging contaminants
 - Medium - high K_{OW}
 - Triclosan, triclocarban, perflourinated compounds, flame retardants

Selected References and Websites

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- Priority Pollutants: <http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>
- Canadian Environmental Quality Guidelines: <http://cegg-rcqe.ccme.ca/>

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