Case Study: USEPA Benthic Invertebrate Risk Assessment for Endosulfan

Presentation to:

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Risk Assessment for the Sediment Compartment

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Topics

1. **Background**
   - Overview of OPP Aquatic Ecological Risk Assessment
   - Considerations for Requiring Sediment Toxicity Testing

2. **Endosulfan Case Study**

3. **Conclusions and Lessons Learned**

OPP Aquatic Ecological Risk Assessment Overview

1. **'Tiered' process based on USEPA Ecological Risk Assessment Guidelines (1998)**
   - Tier 1 = simple, upper bound risk estimates
   - Tier 2 = more refined (region/crop-specific; but still "high end")
   - Tier 3 = most refined, site-specific, often probabilistic

2. **Problem Formulation:**
   - Where key exposure pathways, receptors of concern and data needs are identified & analysis plan is formulated

3. **Exposure Assessment :**
   - Model-based exposures reflect high end estimates from 30-yr simulations of daily concentrations (overlying water, pore water, sediment) considering:
     - Chemical fate properties
     - Soil properties
     - Meteorological data
     - Application rate/method and crop
   - Monitoring data also used for comparison and assessment

OPP Aquatic Ecological Risk Assessment (Overview)

4. **Effects Assessment:**
   - **Required aquatic toxicity tests (outdoor uses):**

Taxa	Acute	Subchronic/ Chronic
Fish	2 fw, 1 sw	1 fw, 1 sw
Inverts. (water column)	1 fw, 2 sw	1 fw, 1 sw
Inverts. (sediment)		2 fw, 1 sw
Plants		4 algae, 1 vascular

   - Data from scientific literature also evaluated
   - Endpoints: acute (LC_{50}/EC_{50}); Chronic (NOAEC)

5. **Risk Characterization:**
   - Deterministic (Risk Quotient): *Estimated Exposure Concentration* / *Toxicological Effect Concentration*
   - Probabilistic: *Distribution of Exposure Concentrations* / *Distribution of Effect Concentrations*

Rationale for Sediment Toxicity Testing

1. **Integrates multiple exposure routes**
   - respiration of pore water & overlying water
   - ingestion of sediment & food
   - dermal uptake

2. **Accounts for factors affecting chemical bioavailability**
   - differences in organic carbon quality
   - influence of other sorption matrices
   - non-equilibrium conditions

Rationale for Sediment Toxicity Testing (Cont'd)

3. **Broader consideration of chemical sensitivity among invertebrate taxa**

Neonicotinoid	*D. magna* (mg/L)	*C. riparius* (mg/L)	Ratio
Clothianidin (48-h EC_{50})	>119	0.022	>5,400
Clothianidin (NOAEC)	0.12 (21-d)	0.0011(10d, p.w.)	100
Imidacloprid (48-h EC/LC_{50})	85	0.069	1,200
Thiamethoxam (48-h EC_{50})	>106	0.035	>3000

Source: USEPA, OPP, EFED Ecotoxicity Database (accessible at: http://www.ipmcenters.org/Ecotox/)

Pyrethroid	*D. magna* 48-h EC_{50} (µg/L)	*H. azteca* 96-h LC_{50} (µg/L)	Ratio
Permethrin	0.32	0.021	15
Cyfluthrin	0.16	0.0023 (g.m.)	70
Cypermethrin	0.147	0.0027 (g.m.)	54
Bifenthrin	1.6	0.0065 (g.m.)	250
λ-Cyhalothrin	0.013	0.0023 (g.m.)	6

Source: CRWQB-SF Pyrethroid Water Quality Criteria Documents

Sediment Toxicity Testing in OPP

1. **Three studies are currently required when certain conditions are met**
   - **Freshwater:** ***Hyalella azteca, Chironomus dilutus***
   - **Saltwater:** ***Leptocheirus plumulosus (Ampelisca abdita, Eohaustorius estuarius, Rhepoxynius abronius)***
2. **Endpoints = survival, growth (10-d), development rate, reproduction (28-65d)**
3. **Spiked sediment design with equilibration**
4. **Concentrations measured in pore water, sediment, overlying water**

Draft Conceptual Framework for Considering Sediment Toxicity Testing

Example Considerations

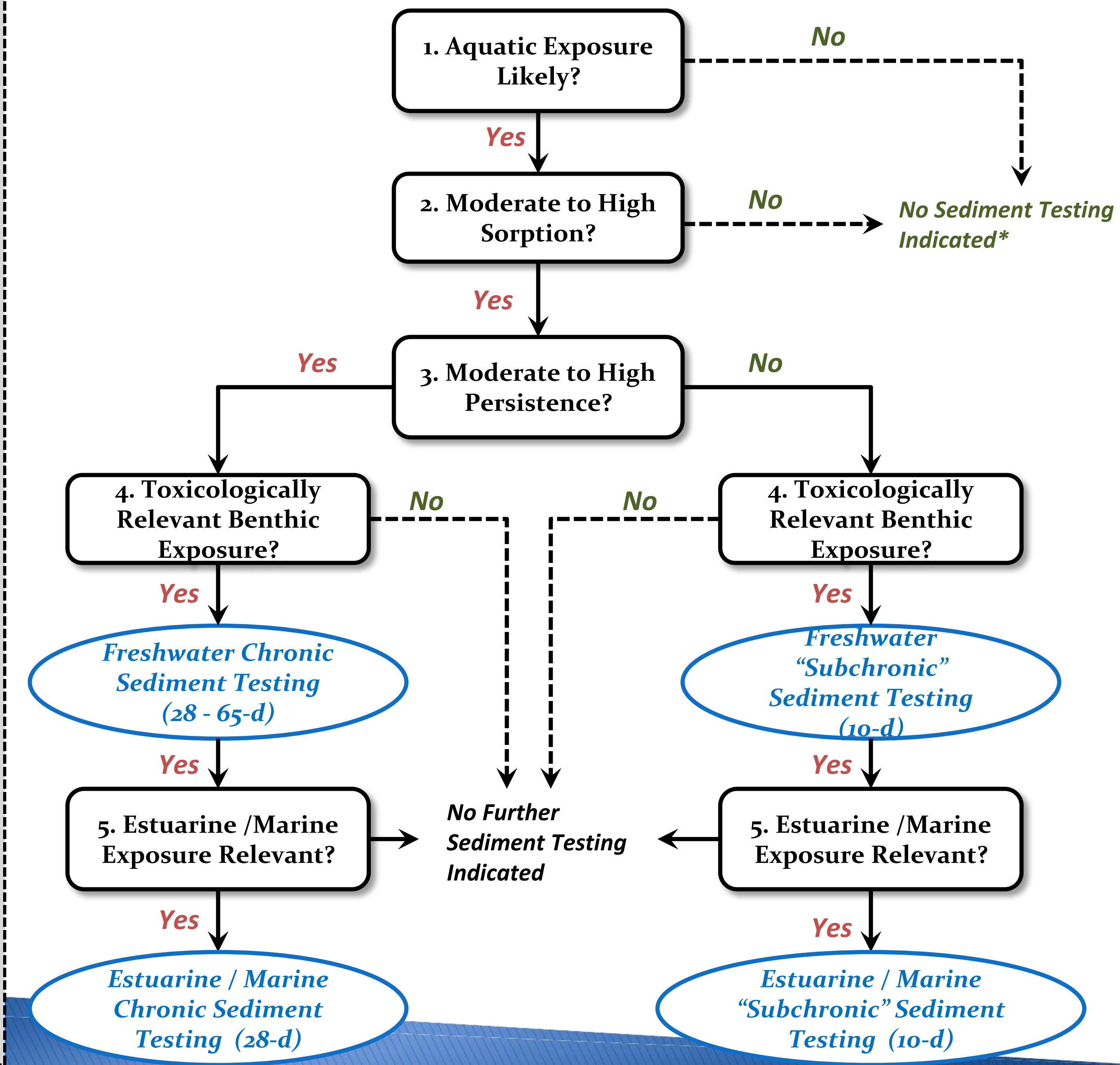
1. Outdoor Use Pattern

2. K_{oc} >1000, K_d >50, Log K_{ow} >3

3. Aerobic soil/aquatic metabolism $T_{1/2}$ > 10d

4. Exposure vs. Toxicity

5. Exposure Potential in Estuarine/Marine Environment

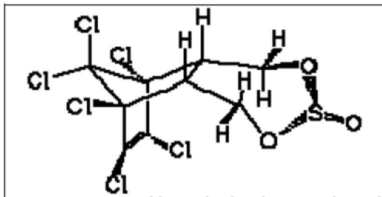


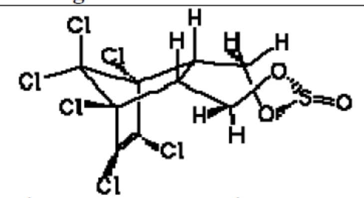
Endosulfan Case Study:

EPA United States Environmental Protection Agency

Office of Chemical Safety and Pollution Prevention

Endosulfan:
2010 Environmental Fate and Ecological Risk Assessment

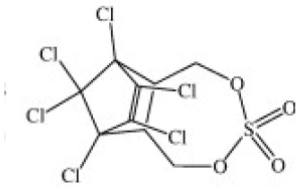




(the wedge bonds are used to indicate direction, not stereo-isomerism)

α-endosulfan (CAS: 959-98-8) **β-endosulfan** (CAS: 33213-65-9)

http://www.alanwood.net/pesticides/index_cn_frame.html



endosulfan sulfate (CAS: 1031-07-8)

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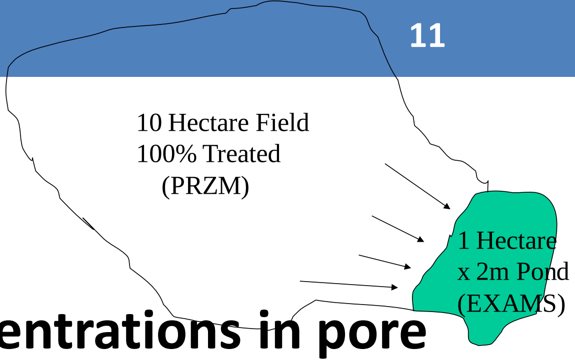
http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2002-0262-0162;oldLink=false

Problem Formulation:

- Organochlorine insecticide used on wide variety of crops in U.S. (<2010)
- Stressors of concern include two parent isomers (α & β) and primary degradate (endosulfan sulfate)
- Neurotoxic MOA (blockage of GABA-gated chloride channels)

Parameter	*α-Endosulfan*	*β-Endosulfan*	Endosulfan Sulfate
Water Solubility (μg/L)	530	280	330
Log K_{OW}	4.7	4.8	3.7
K_{OC} (*L/kg-OC)*	10,600	13,500	n/a
Hydrolysis Half Life	pH 5: >200 d pH 7:11 d	pH 5: >200 d pH 7:19 d	pH 7:184 d
Aerobic Soil Metabolism Half Life	35-67d	104-265d	Stable
Anaerobic Soil Metabolism Half Life	105-124 d	136-161 d	125-165 d

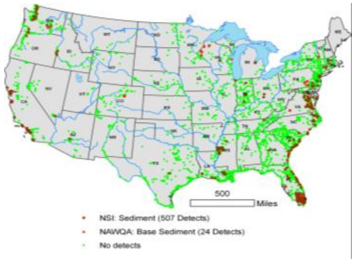
Exposure Assessment:



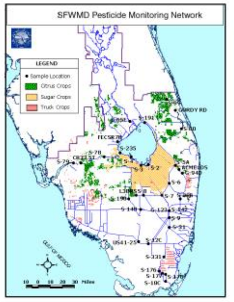
Modeled Concentrations:

- PRZM/EXAMS model used to estimate concentrations in pore water and sediment using “standard pond” (30 yrs)
- Freely dissolved chemical in pore water estimated using EqP, Koc, DOC and foc
- EEC = 21-d avg. concentration with 1-in-10 yr return frequency
- Max. EEC = 2.99 µg/L (pore water); 35.6 mg/kg-oc ($\alpha+\beta+SO_4$)

Monitored Concentrations:



- Two national-scale programs (USGS-NAWQA & NSQI)
  - ~ 10,000 measurements; 1990 – 2007; α &β only
  - detection rate = 2-6%; max. = 430 mg/kg dw (α);
- 1 local “targeted” program (SFWMD)
  - 190 samples; 1992-2008; α, β & SO_4
  - frequent detection (C-111 canal); max. = 152 mg/kg dw



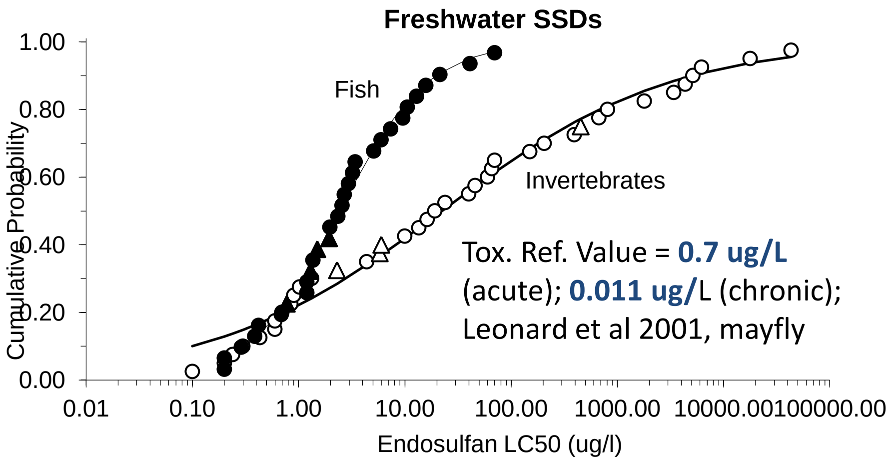
Effects Assessment:

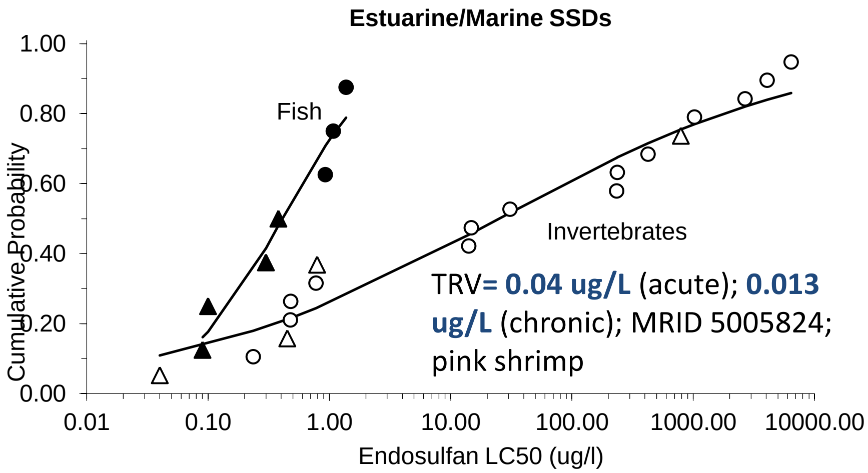
Sediment Toxicity Data

- Midge (*C. dilutus*): 10-d & 50-d spiked sediment, endosulfan sulfate
- Amphipod: (*L. plumulosus*): 10-d and 28-d spiked sediment, endosulfan sulfate

Species	*Pore water*	*Sediment (dw)*	Sediment (OC)
C. dilutus (50-d NOAEC, emergence, survival)	0.35 ug a.i./L	0.17 mg/kg	1.8 mg/kg-oc
L. plumulosus (28-d NOAEC, growth, reproduction)	1.58 ug a.i./L	0.48 mg/kg	10.2 mg/kg-oc

Water column Toxicity data





Risk Characterization:

Sediment Toxicity Data (chronic)

Pore water RQ = $\frac{\text{21-d EEC (µg a.i./L-pw)}}{\text{NOAEC (µg a.i./L-pw)}}$

Sediment RQ = $\frac{\text{21-d EEC (µg a.i./kg-oc}}{\text{NOAEC (µg a.i./kg-oc)}}$

Monitoring –based Sediment RQ = $\frac{\text{Max. Obs. Conc.(µg a.i./kg-oc}}{\text{NOAEC (µg a.i./kg-oc)}}$

Water Column Toxicity Data

Acute pore water RQ = $\frac{\text{Peak EEC (µg a.i./L-pw)}}{LC_{50}\text{ (µg a.i./L- water column)}}$

Chronic pore water RQ = $\frac{\text{21-d EEC (µg a.i./L-pw)}}{\text{NOAEC (µg a.i./L- water column)}}$

Risk Findings (Max EEC):

Exposure Basis	Toxicity Basis	Freshwater RQ		Saltwater RQ	
		Acute	*Chronic*	*Acute*	*Chronic*
1. Pore water, model	Pore water measured	---	8.5	---	1.9
2. Sediment OC, model	Sediment OC, measured	---	19.5	---	3.5
3. Pore water, model	Water column, measured	4.3	270	76	230
4. Sediment OC, monitored	Sediment OC, measured	---	2.4 - 11.8 (1)	---	---

(1) RQ values of 2.4 and 11.8 correspond to assumed TOC in sediment of 10% and 2%, respectively

Observations:

- Method of RQ calculation did not alter overall risk conclusions for max. EEC.
- **Methods 1 vs. 2:** OC-based RQ is 2X pw-based RQ; may reflect differences in modeled vs. observed K_{OC} and/or bioavailability
- **Methods 1 vs. 3:** Much higher RQ values using water column toxicity endpoints; Greater number of species; uncertainty in ACR extrapolation
- **Method 4:** Max. Value from monitoring data corroborate modeled risk estimates assuming 2-10% OC

Conclusions & Lessons Learned

1. Since 2007, USEPA/OPP has been formally requesting sediment toxicity testing for pesticides
2. Value of sediment toxicity testing: incorporating multiple exposure routes & broadening the diversity of aquatic invertebrates tested
3. Multiple approaches are available for estimating risk to benthos that vary in the medium for estimating exposure and effects
4. Current thinking is to assess benthic invertebrate risk using multiple methods, keeping in mind their relative strengths and weaknesses
5. Some Current challenges:
   A. Identifying ‘optimal’ battery of sediment toxicity tests
   B. Bioavailability
   C. Analytical methods
   D. Statistical power

THANK YOU For Your Attention!

QUESTIONS?