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Northeast Waste Management Official's Association

Interstate Technology Regulatory Council's Guidance on:

Incorporating Bioavailability Considerations into the Evaluation of Contaminated Sediment Sites (CS-1, 2011)

Presented by: Stephen Clough, Ph.D., DABT, Haley & Aldrich, Inc.

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ITRC Web-based Guidance Outline

- Introduction and background on bioavailability
- Overview of bioavailability processes
- Bioavailability pathway exposure assessment
  - Screening
  - Background
  - Pathway exposure assessment
    - Benthic invertebrates
    - Fish and water column invertebrates
    - Wildlife
    - Plants
    - Human health
- Risk management decision-making

http://www.itrcweb.org/contseds-bioavailability/

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ITRC Sediments Team

- **States**
  - Alabama
  - California
  - Delaware
  - Florida
  - Kentucky
  - Michigan
  - New Jersey
  - New York
  - Oklahoma
  - Oregon
  - Pennsylvania
  - Texas
  - Washington
- **Universities**
  - Purdue
  - U. of Florida
  - U of Texas
- **Federal Agencies**
  - Navy
  - Army
  - AFCEE
  - EPA Including Region 2 & 5
  - USACE
  - DOE
- **Community Stakeholders**
  - Mtn Area Land Trust
  - AAEJC
- **Industry**
  - AMEC
  - Alta Environmental
  - AECOM
  - AFMC
  - Alcoa
  - Arcadis
  - Battelle
  - Beacon
  - Brown and Caldwell
  - Bootheel LEPC
  - Burns & McDonnell
  - BP
  - CDM CH2MHill
  - CETCO
  - Columbia Analytical
  - DuPont Geosyntec
  - EMCBC
  - Environ
  - ExxonMobil
  - Haley & Aldrich, Inc
  - Kleinfelder
  - Langan Engineering
  - LATA-Kemron
  - Malcolm Pirnie
  - M.W. Global
  - MWH
  - RegTech
  - Neptune and Co.
  - SAIC W.L.
  - Gore
  - SRNL
  - Test America labs
  - Tetra Tech
  - URS
  - WRI
  - SPAWAR
  - SSC
  - Shell

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What You Will Learn from the ITRC Bioavailability Guidance…

The intended users of this guidance are individuals who have a working knowledge of contaminated sediment management but seek additional information about bioavailability.

- What is bioavailability?
- When do we apply bioavailability adjustments?
- What are the available tools and how do we use them?
- How do we use the information to make risk management decisions?
- You will **NOT** learn how to conduct a Risk Assessment that incorporates bioavailability.

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What is Bioavailability?

"…individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediment (National Research Council, 2003)."

Specifically, bioavailability addresses the fact that only a fraction of the contaminant concentration present in the environment may be taken up or result in an effect on an organism!

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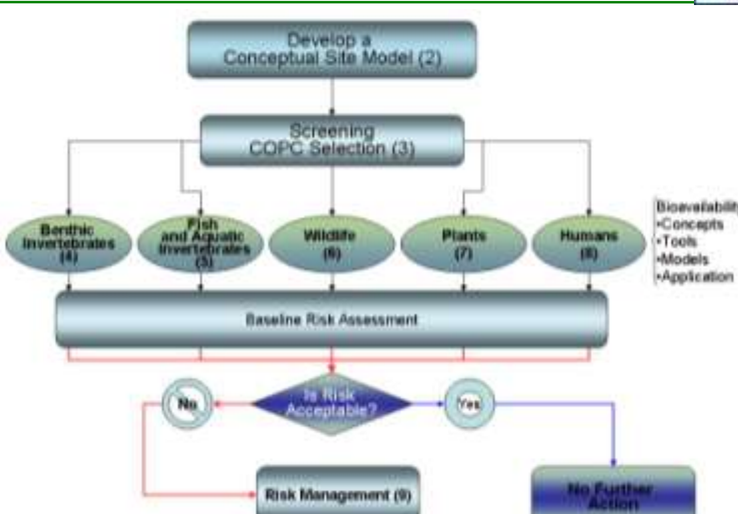
Contaminated Sediment Assessment Approach



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Scoping Your Site….Chapter 2

- Site history
- Site boundaries (extent of contamination)
- Contaminants of potential concern (COPC)
- Conceptual site model (CSM)

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Processes to Consider During Scoping

Physical

- **Bed Transport**
- **Deposition/ Resuspension**
- **Bioturbation**
- **Advection/diffusion**
- **Grain size COPC distribution**
- **Burial**
- **Temperature**

Chemical

- **Sorption/desorption**
- **Transformation/ degradation**
- **Geochemical (TOC, salinity, pH, Redox)**

Biological

- **Uptake**
- **Biotransformation**
- **Bioaccumulation**
- **Mode of action**
- **Critical body burden**

Caution – Sediment are mixtures

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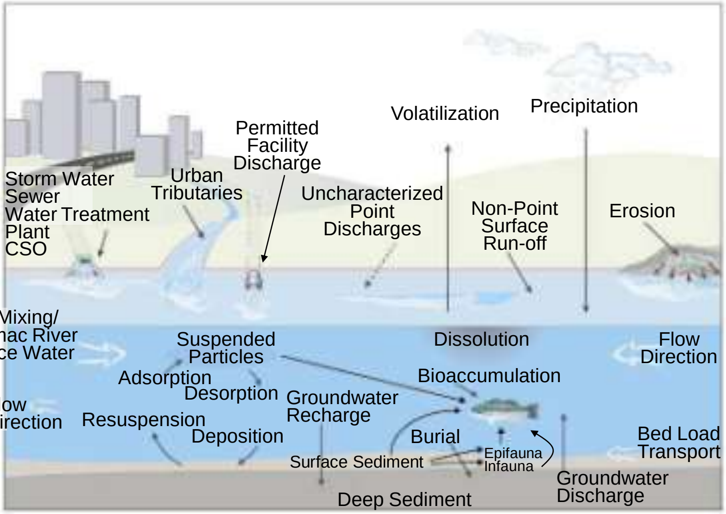
Example Conceptual Site Model
Anacostia River



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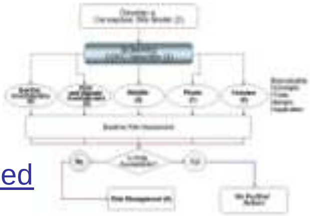
Screening Your Site…Chapter 3

- Screening values are <u>not</u> site specific
- Conservative values
  - Levels below which there is a good probability there is low risk
  - Values above screening levels do not imply unacceptable level of risk
- Determine if there is a need for further investigation



<u>Screening values have been established</u>

- Beware – know how your screening levels were derived! (McDonald 2000)

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Screening and Bioavailability

- Know urban/suburban “background” concentrations or “local conditions”.
- Normalization of bulk sediments (Section 3.0) can be applied within the screening process under some state regulatory programs
  - Example: 7 mg PCB/kg sediment ÷ 0.035 kg TOC/kg = 200 mg PCB/kg TOC
- However the assessment of site impacts is improved by incorporating bioavailability in later stages of the site investigation using site-specific considerations

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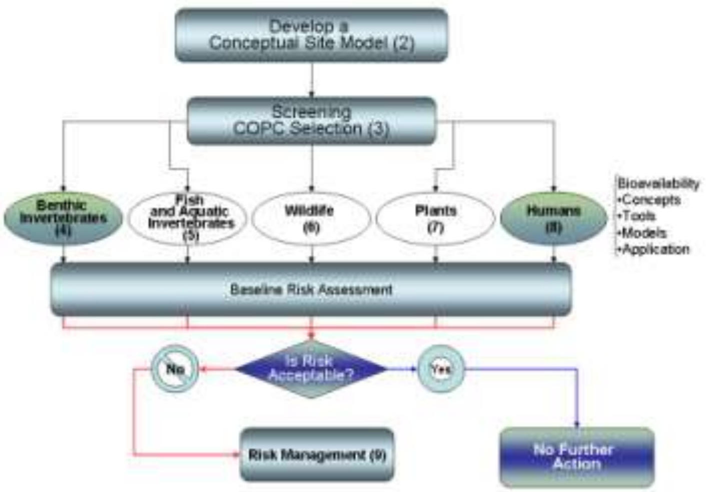
Most Common Exposure Pathways



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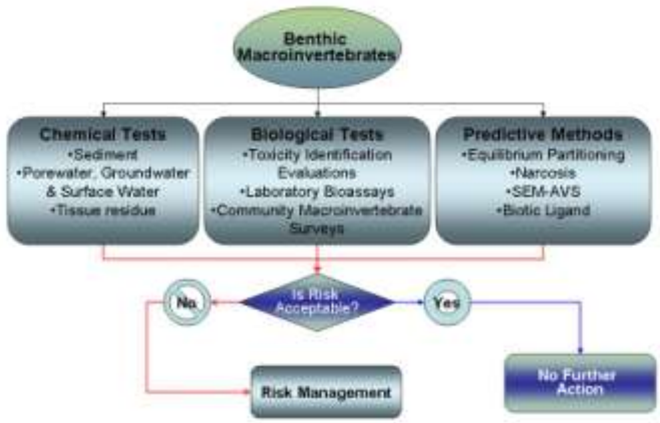
Benthic Pathway…Chapter 4



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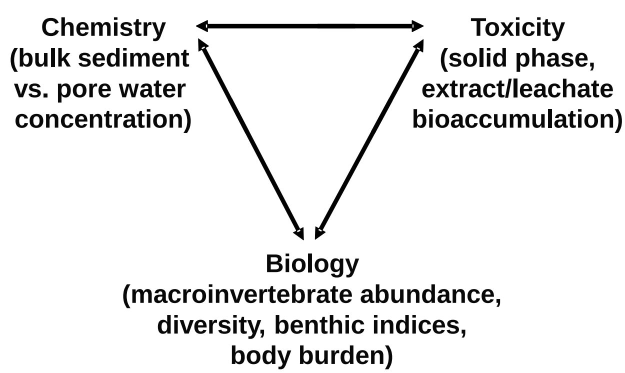
Procedures for Assessing Bioavailability to Benthic Invertebrates

- Sediment Quality Triad (SQT):



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Acid Volatile Sulfide Reduces Metal Bioavailability in Sediment

Most sediments are ANOXIC ⟶

$$SO_4^{2-} + COD \xrightarrow{\text{sulfate reducing bacteria}} HS^- + CO_2$$

sulfate | organic substrate | sulfate reducing bacteria | sulfide | carbon dioxide

$$S^{-2} + Fe^{2+} \rightarrow FeS$$

Metal Sulfide	$Log_{10}K_{sp,2}$[a]	$Log_{10}K_{sp}$[b]	$Log_{10}(K_{MeS}/K_{FeS})$
FeS	−3.64	−22.39	—
NiS	−9.23	−27.98	−5.59
ZnS	−9.64 **10^6 X stronger**	−28.39	−6.00
CdS	−14.10	−32.85	−10.46
PbS	−14.67	−33.42	−11.03
CuS	−22.10 **10^{18} X stronger**	−40.94	−18.55
Ag_2S	−36.14	−54.71	−32.32

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Iron Sulfides in Natural Sediment

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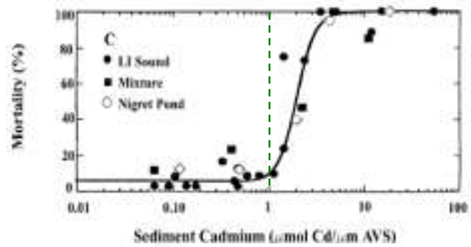
Tools to Assess the Benthic Pathway; Chemical – Metal Binding by AVS

- SEM/AVS
  - Simultaneously Extracted Metals/ Acid Volatile Sulfides

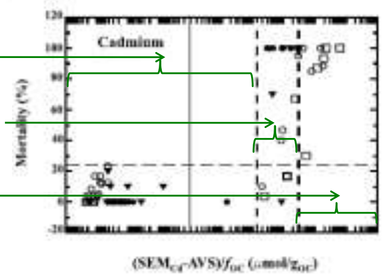


- SEM-AVS/f_{OC}

No Toxicity
(<130 umoles/goc)

Toxicity Uncertain
(130 – 3000 umoles/goc)

Toxicity
(>3000 umoles/goc)



From EPA-600-R-02-011, 2005

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How Do You Sample for AVS/SEM?

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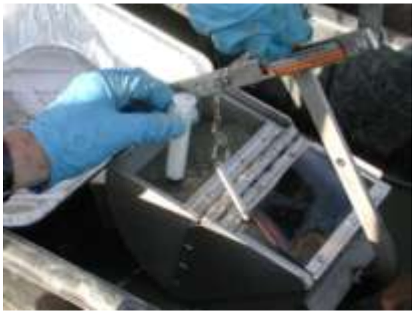
How Do You Sample for AVS/SEM?



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How Is AVS and SEM Measured?

- 1 – 10 g sediment in 120 ml deionized water
- Add 6 N HCl
- Trap "acid volatile sulfide" and measure
- Quantify "simultaneously extracted metals" (dissolved): Cd, Cu, Ni, Zn, Pb, Ag
- Measure using ICP-MS

Allen HE, Fu G, Deng B. 1993. E*nviron. Toxicol. Chem. 12:1-13*

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AVS and SEM Laboratory Reports Provide Easy Interpretation

SAMPLE RESULTS

Lab ID:	L1101545-13	Date Collected:	02/01/11 13:47
Client ID:	G-32-0.0	Date Received:	02/04/11
Sample Location:	Not Specified	Field Prep:	Not Specified
Matrix:	Soil		
Percent Solids:	39%		

Parameter	Result	Qualifier	Units	RL	MDL	Dilution Factor	Date Prepared	Date Analyzed	Prep Method	Analytical Method	Analyst
Acid Volatile Sulfide w/Simultaneously Extracted Metals - Mansfield Lab											
Sulfide, Acid Volatile	19.1		umoles/gm	0.728	–	1	02/14/11 08:00	02/14/11 08:00	36,-	36,-	LR
Cadmium, Total	0.00121		umoles/gm	0.00104	–	1	02/14/11 08:00	02/21/11 11:33	36,-	1,6020A	LR
Copper, Total	0.3820		umoles/gm	0.0738	–	1	02/14/11 08:00	02/21/11 11:33	36,-	1,6020A	LR
Lead, Total	0.10800		umoles/gm	0.01130	–	1	02/14/11 08:00	02/21/11 11:33	36,-	1,6020A	LR
Nickel, Total	0.2430		umoles/gm	0.0398	–	1	02/14/11 08:00	02/21/11 11:30	36,-	1,6020A	LR
Zinc, Total	0.7380		umoles/gm	0.0714	–	1	02/14/11 08:00	02/21/11 11:33	36,-	1,6020A	LR
SEM/AVS Ratio	0.076		umoles/gm	0.064	NA	1	02/14/11 08:00	02/21/11 11:30	36,-	1,6020A	LR

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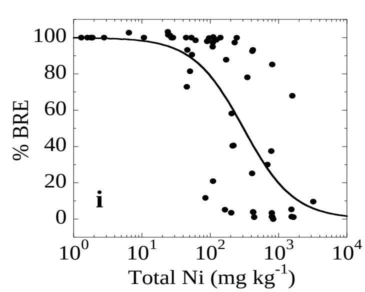
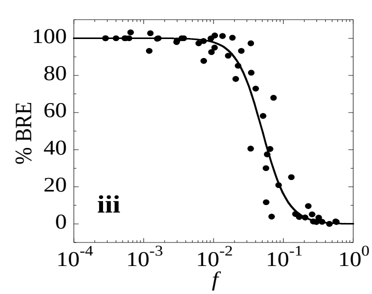
Tools to Assess the Metals Bioavailability in Soils (not in Guidance)

- Root elongation tests (lettuce, barley)

Total Ni



Biotic Ligand Model



Thakali, S., Allen, H. E., Di Toro, D. M., Ponizovsky, A. A., Rooney, C. P., Zhao, F.-J., and McGrath, S. P. "A terrestrial biotic ligand model I: Development and application to Cu and Ni toxicities to barley root elongation in soils." Environ. Sci. Tech., 40(22) (2006): 7085-7093.

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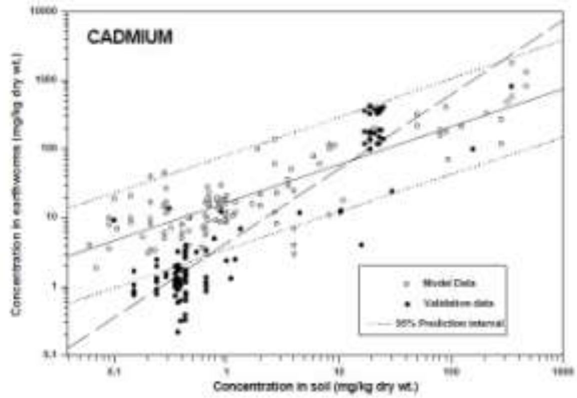
Tools to Assess the Metals Bioavailability in Soils (not in Guidance)

- Earthworm bioaccumulation tests



Sample, BE, Beauchamp, JJ, Efroymson, RA, Suter, GW, and Ashwood, TL, 1998. Development and Validation of Bioaccumulation Models for Earthworms. Oak Ridge National Laboratory, Environmental Restoration Program, ES/ER/TM-220. rais.ornl.gov/documents/tm220.pdf

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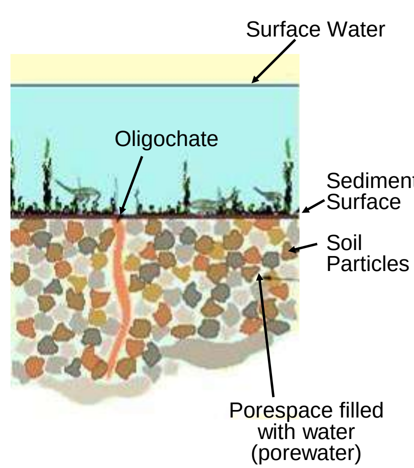
Tools to Assess the Benthic Pathway; Chemical - Porewater

- Porewater (Direct)
  - Centrifugation (lab)
  - Syringes/suction devices
  - Piezometers
  - Ultraseep/Trident probe
  - SPME (solid phase microextraction; EPA SW-846 8272; ASTM D73-63-07)
- Porewater (Indirect)
  - Peeper
  - SPMD (semi-permeable membrane device) / dialysis bags
  - Diffusion in thin films
  - SPME, POM (Polyoxymethylene) film, PE (Polyethylene) strips
  - GORE® Module
  - Diffusive flux

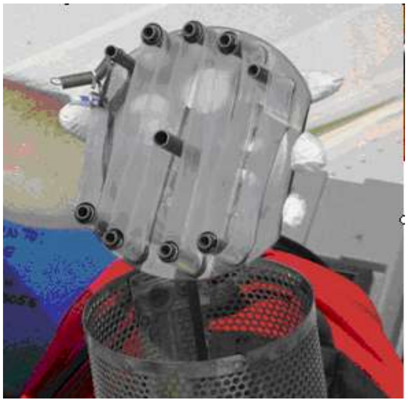


25 **Tools to Assess the Benthic Pathway; Chemical - Porewater (Direct) – Suction Devices**

Airstone "Before"

Airstone "After"

26 **Tools to Assess the Benthic Pathway; Chemical - Porewater (Indirect) – Semipermeable Membrane Devices**



SPMD "Before"

SPMD "After"

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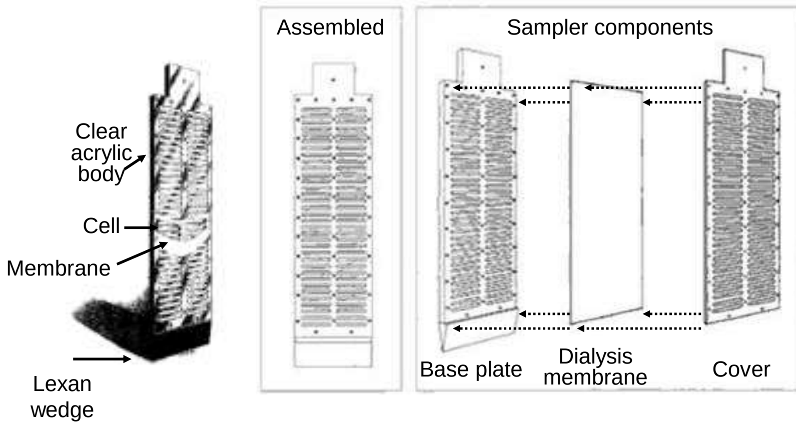
Tools to Assess the Benthic Pathway; Chemical - Porewater (Indirect) – "Peepers"



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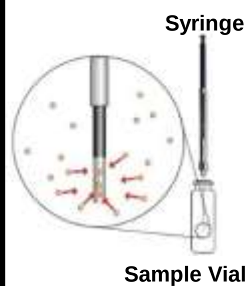
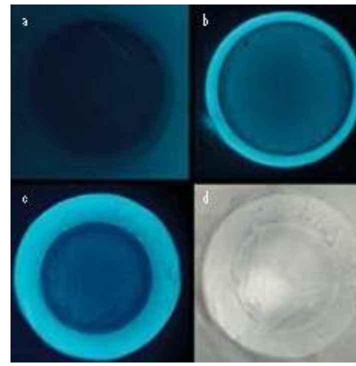
Tools to Assess the Benthic Pathway; Chemical - Porewater (Indirect) – "Peepers"

Photographs courtesy of A. Lee Gustafson, Net Zero LLC

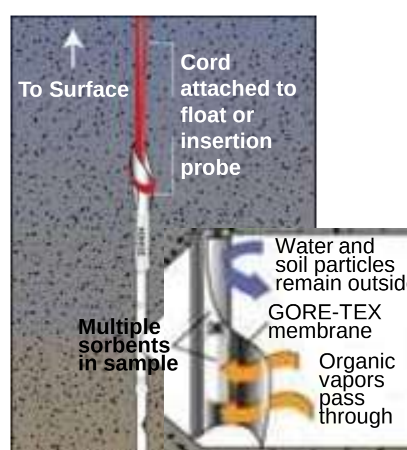
29 **Tools to Assess the Benthic Pathway; Chemical - Porewater (Direct/Indirect) – SPME (Solid Phase Micro Extraction)**





30 **Tools to Assess the Benthic Pathway; Chemical - Porewater (Indirect) – GORE® Module**

- Screening tool that can be used to sample porewater
- Measure concentrations in GORE lab only
- Verified use in groundwater
- Effective for VOCs



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Tools to Assess the Benthic Pathway; Biological - Sediment Toxicity Tests

Hyalella azteca

FRESHWATER

Chironomus dilutus

Neanthes arenaceodentata

BRACKISH OR SALTWATER

Eohaustorius estuarius

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Tools to Assess the Benthic Pathway; Biological - Macroinvertebrate Surveys

"Pollution Sensitive"

"Pollution Tolerant"

Benthic Metrics: Abundance, Richness, %EPT, %Dominance, %Chironomids, Hilsenhoff's or Shannon-Weiner Diversity Indices

33 **Tools to Assess the Benthic Pathway; Biological - Minimally Disturbed Stream**

1 inch

Photos courtesy of Susan Davies, Maine DEP

34 **Tools to Assess the Benthic Pathway; Biological - Stream Adjacent to Shopping Mall**

1 inch

Photos courtesy of Susan Davies, Maine DEP

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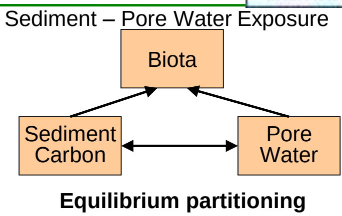
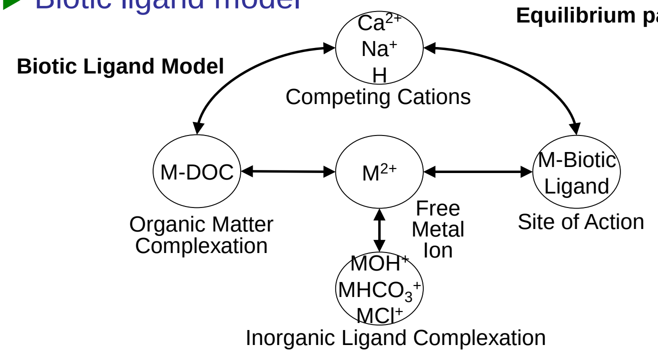
Tools to Assess the Benthic Pathway
Predictive

- Equilibrium partitioning
- Narcosis model
- SEM-AVS/f_{OC}
- Biotic ligand model





Tipping, 1994

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Case Study Using the Benthic Pathway
Tectronix Wetlands Beaverton, OR

- Historic operations → sediment metals exceeding Oregon Department of Environmental Quality (DEQ) Level II screening level values
  - Assessed chemistry, toxicity, SEM/AVS,TOC
    - Maximum (SEM-AVS)/f_{oc} was ~10x less than EPA's adverse effect level
  - Toxicity tests
    - Hyalella azteca mortality
    - Chironomus dilutus growth
    - No adverse effect on amphipods or midges
- Assessment concluded concentrations did not pose potential risks to benthic community
- NFA for stretch of Beaverton Creek based on
  - Results from bulk sediment chemistry
  - Toxicity testing
  - Comparison to (∑SEM-AVS)/f_{OC} toxicity threshold

Photo courtesy Kathleen Hurley

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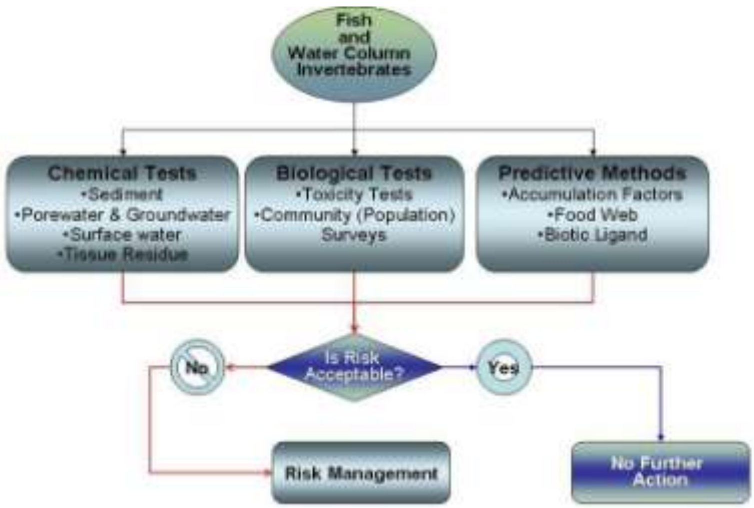
Fish and Water Column Invertebrates Pathway…Chapter 5



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Tools to Assess the Fish and Water Column Invertebrates Pathway Chemical

- Measure water quality above sediment bed → compare to
  - National recommended water quality concentration
  - State water quality standards
- Measure water and tissue residues → compare to
  - Bioaccumulation Factors (BAF)
  - If no BAF → USEPA “EPI Suite” (Estimation Programs Interface)
  - Critical Body Burden (CBB): ~2.5 umol/g wet weight
  - Toxicity Reference Values (TRV)
- Measure Biota-sediment accumulation factors (BSAFs) = $[COPC_{tissue}/f_{lipid}] / [COPC_{sed}/f_{OC}]$
  - <1 or >1?
  - U.S. Army Corp of Eng or ORD BSAF Dbase

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Case Study Using the Fish and Water Column Invertebrates Pathway

McCormick and Baxter Superfund Site, OR

- Residual creosote-derived contaminants including PAHs and dioxins
- Assessments
  - Sediment chemistry
  - Bioassays
  - Tissue residues in fish and crayfish
  - Fish histopathology
- Results
  - Sediment chemistry and toxicity testing
    - Indicated area of the Willamette River - likely to be toxic
  - Tissue residues for PAHs were low in
    - Crayfish (Pacifastacus leniusculus)
    - Large scale sucker (Catastomus macrocheilus)
    - Examination of 249 fish livers found no statistical differences between the site and upstream locations
- ROD required placement of an impermeable cap, based on
  - Sediment chemistry and bioassay data
  - Continuing NAPL discharges from sediments to Willamette River

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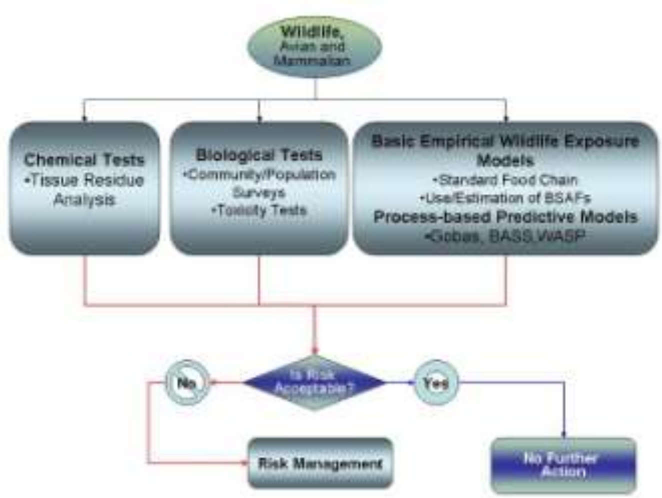
Wildlife Pathway…Chapter 6



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Tools to Assess the Wildlife Pathway: Indirect Measures

- Wildlife effects (already known)
  - Bulk sediment (mg/kg)
  - Literature BAFs
  - Percent of diet
- Calculate: dose (mg/kg/day)
- Compare: to Toxicity Reference Value (TRV)
- Pass?
  - Yes → NFA
  - No → SLERA/BERA
- Exposure/effect: bioaccessibility in sediment

Freshwater (Mallard)

Saltwater (Sandpiper)

Dose $_{(mg/kg/day)}$ **= % Sediment (in diet)**

C_{SED} **(mg/kg) x** $\%_{diet}$ **(kg/day) = mg/kg/day**

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Tools to Assess the Wildlife Pathway; Indirect Measures

- Physiologically-Based Extraction Tests

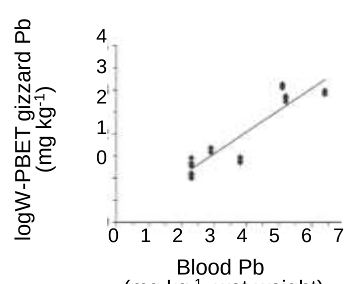

Photo courtesy of Nick Basta, Soil & Envir. Chemistry, Ohio State Univ.

Furman et al., J. Environ. Qual. 35: p. 450 https://www.soils.org/publications/jeq/articles/36/3/899

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Questions & Answers