



August 22, 2013

GEC Session 44

Bioavailability Considerations in Sediment

# Overview on Bioavailability Considerations for Remedial Decision-Making to Protect Ecological Organisms

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# Overview

- Why is bioavailability important to consider and to what chemicals does it apply?
- History of guidance development within EPA
- Example of the how the guidance is applied



# Why is Bioavailability Important?

- Appropriate risk management decisions
  - Protect human health and the environment
  - Avoids unnecessary remediation (mobilize chemicals, destroy habitat, bad for business, bad for stakeholders)
- Chemicals present in non-toxic forms
- “Off the shelf” screening benchmarks
  - First step
  - Exceedance  $\neq$  toxicity
  - Exceedance = investigation



# Which Chemicals?

- Polycyclic aromatic hydrocarbons (PAHs)
- Polychlorinated biphenyls (PCBs)
- Pesticides
- Non-Ionic compounds
  - Benzenes
  - Chlorobenzenes
- Metals
  - Divalent metals (lead, nickel, silver, zinc)
  - Mercury
  - Chromium

*It is reasonable to ask if the chemical is bioavailable before making any final remedial management decision.*



# History and Development

- Bioavailability considerations founded on decades of scientific study
- EPA Guidance not new, could be more widespread
- Use in Georgia is relatively new, more commonly being used, value in decision-making
- Examples of bioavailability considerations
  - Weathering
  - Binding and sequestration (clays, sulfides, organic carbon)
  - Metabolism w/in the food web
  - Water hardness influence
  - Organism characteristics



# Developed because...

- Clean Water Act
- Have water quality criteria based on tox testing

BUT...

- Sediments recontaminate water
- Do not have many sediment criteria because tox testing is difficult to interpret, time consuming, and expensive.

SO...



Great Lakes Region

**Must bridge gap  
between water and  
sediment**



# Evolution 1991 - 2003

*Environmental Toxicology and Chemistry*, Vol. 10, pp. 1541-1583, 1991  
Printed in the USA. Pergamon Press plc

0730-7268/91 \$3.00 + .00  
Copyright © 1991 SETAC

## *Annual Review*

*Environmental Toxicology and Chemistry*, Vol. 13, pp. 157-166, 1994  
Printed in the USA Pergamon Press Ltd

0730-7

United States  
Environmental Protection  
Agency

Office of Research and Development  
Washington, DC 20460

EPA-600-R-02-013  
www.epa.gov



## Procedures for the Derivation

RY FOR  
TED  
ND

EPA/600/R-02/010  
August 2003

## Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Dieldrin



United States  
Environmental Protection  
Agency

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Environmental Protection  
Agency

Office of Research and Development  
Washington, DC 20460

EPA-600-R-02-013  
www.epa.gov

United States  
Environmental Protection  
Agency

Office of Research and Development  
Washington, DC 20460

EPA-600-R-02-011  
www.epa.gov

# Procedure of Equilibrium Sediment for the Organism

# Procedure of Equilibrium Sediment for the Organism (Case Study)

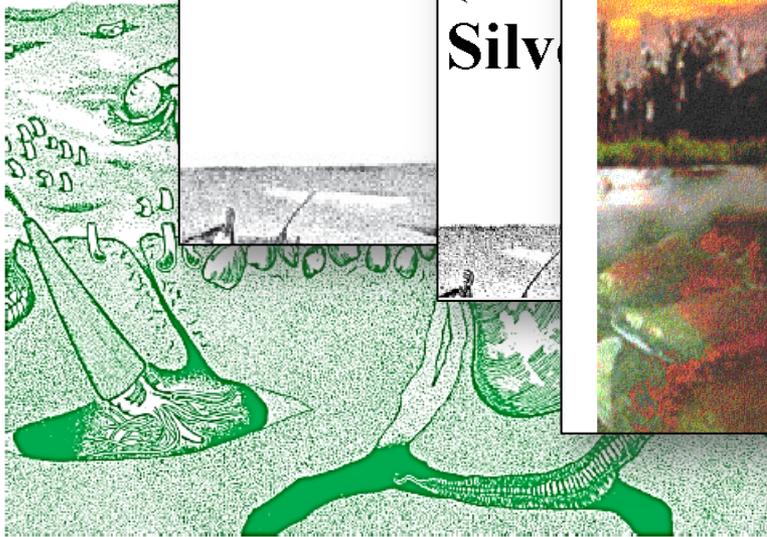


# Contaminated Sediment Remediation



EPA 120/R-07/001 | March 2007  
www.epa.gov/osa

## Framework for Metals Risk Assessment





# Equilibrium Partitioning

- One type of bioavailability consideration  
“EqP”
- Takes into account binding of organics to  
OC
- Generally accepted, moving in to popular  
use

**Uses water criterion + partitioning =  
sediment criterion**

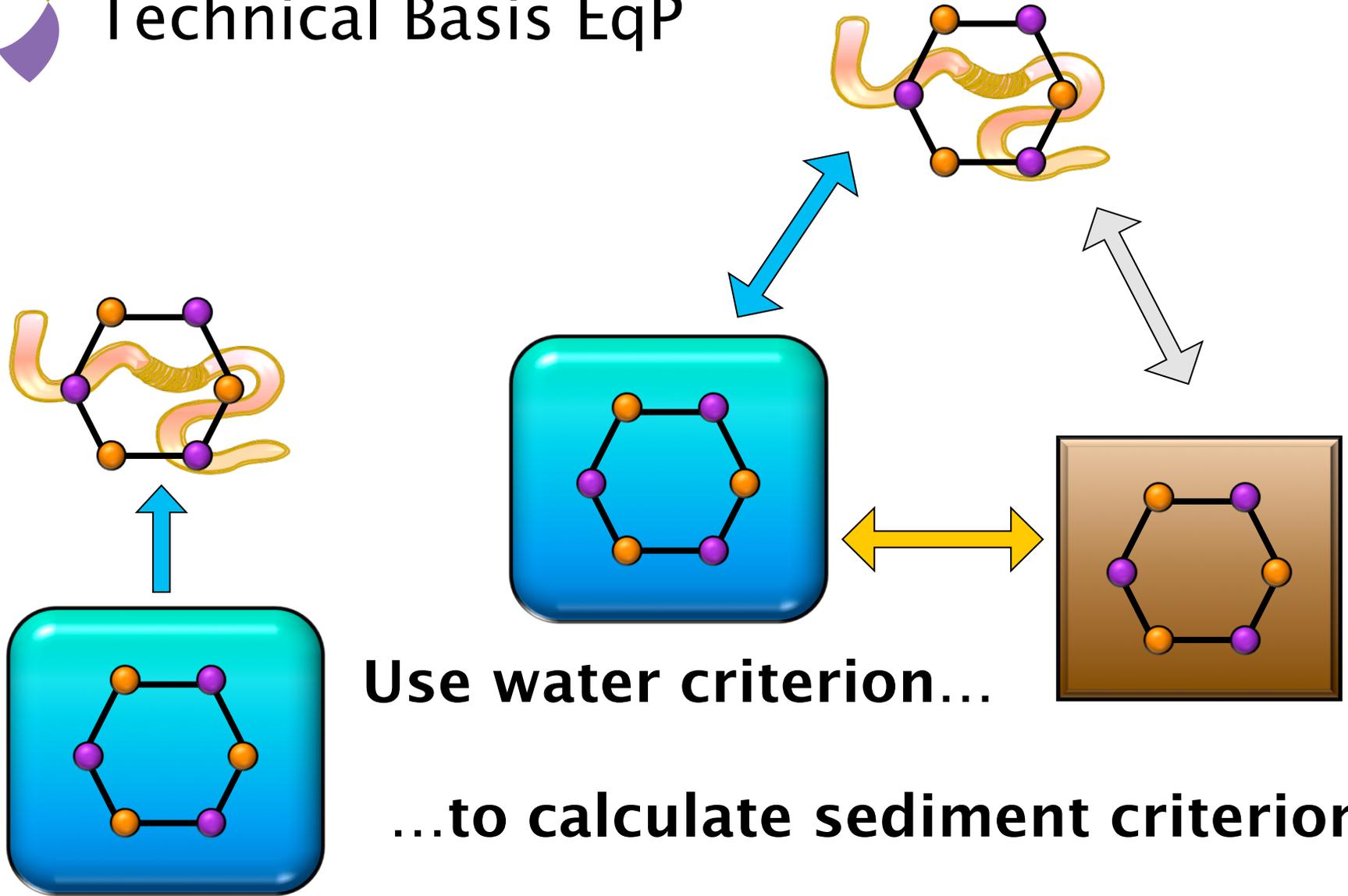


## EqP Built on 3 Observations

- Not all constituents in the sediment are toxic
- Sediment invertebrate sensitivity  $\approx$  water invertebrate sensitivity
- Partitioning models work



# Technical Basis EqP





# Sediment is complex...





Sediment is complex...



**SAND**

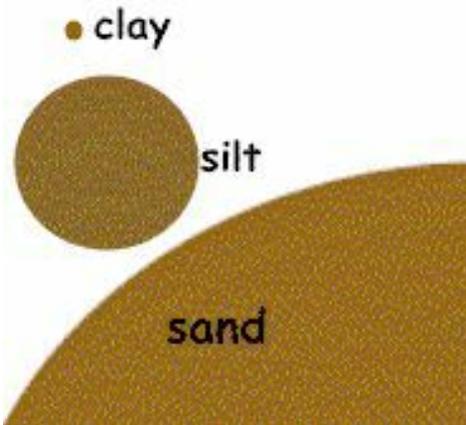




# Sediment is complex...



**SILT  
and  
CLAY**





# Sediment is complex...



- Organic Material
- Rotting plants
  - Microorganisms
  - Decomposition
  - Trash

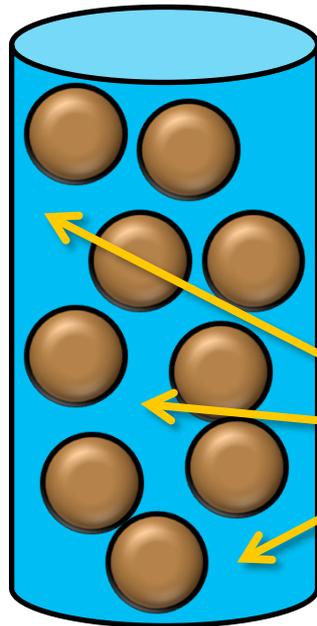
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## ORGANIC CARBON

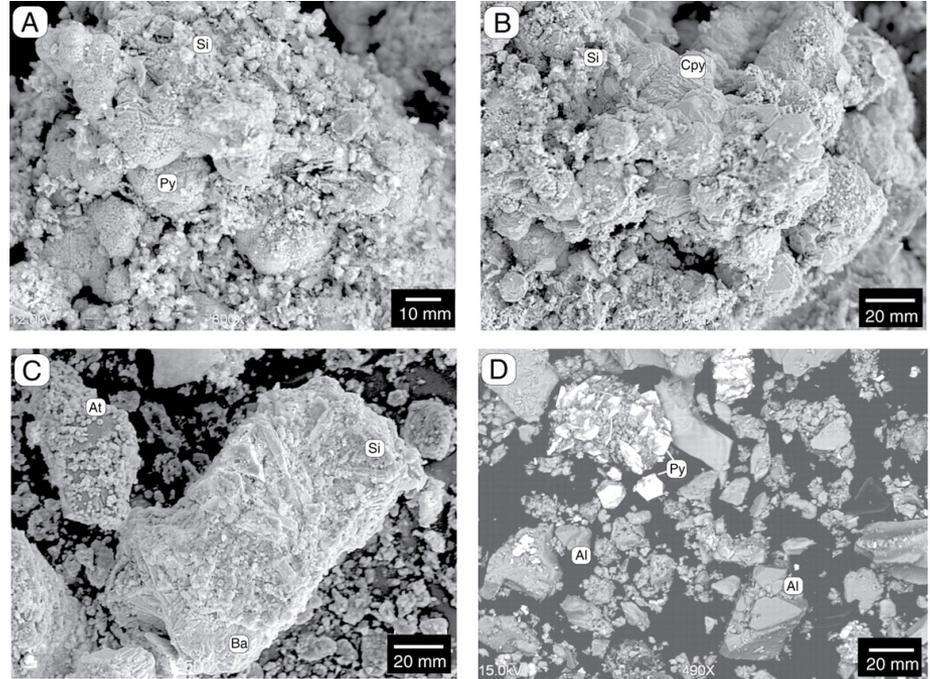




# Sediment is complex...



## Porewater



**Interstitial spaces filled with water**

**Closely associated with sediment**



# EqP Relies on These Assumptions

- Constituents in equilibrium
  - sw – pw – sd
- Main exposure route is pw → organism
  - sd → organism is trivial
- You have “good” data
  - water benchmark
  - partitioning value
  - OC concentration



# USEPA (2008) Criteria for 32 Chemicals

- Benzene
- Biphenyl
- 4-Bromophenyl phenyl ether
- Butyl benzyl phthalate
- Chlorobenzene
- Diazinon
- Dibenzofuran
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- Di-n-butyl phthalate
- Diethyl phthalate
- Ethylbenzene
- Hexachloroethane
- Pentachlorobenzene
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethene
- Tetrachloromethane
- Toluene
- Toxaphene
- Tribromomethane (Bromoform)
- 1, 2, 4-Trichlorobenzene
- 1, 1, 1-Trichloroethane
- Trichloroethene
- m-Xylene
- BHC other than Lindane
- Gamma-BHC, Lindane
- Endosulfan mixed isomers
- Alpha-Endosulfan
- Beta-Endosulfan
- Malathion
- Methoxychlor



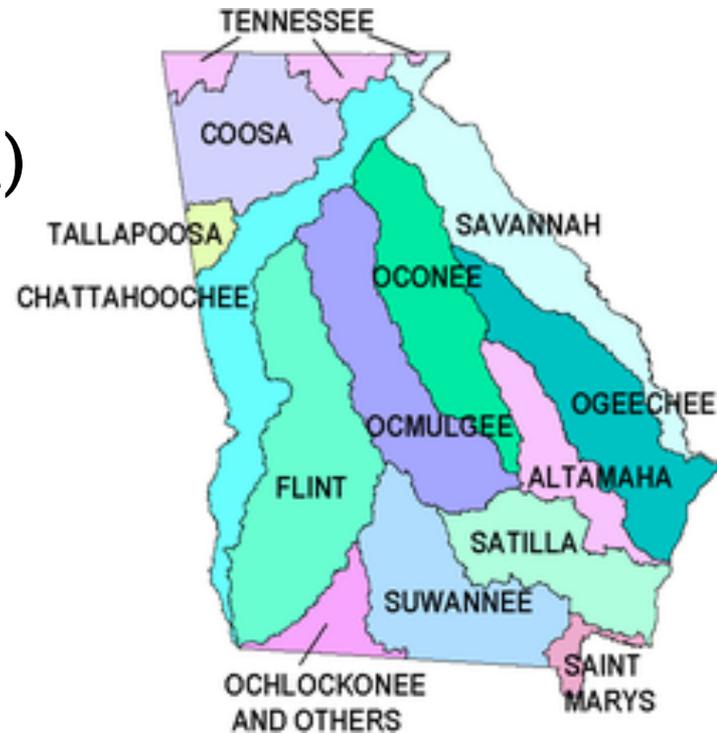
## Data Needs

- Determine appropriate water quality criterion
- Appropriate partitioning value ( $K_{ow}$ )
  - EqP works where  $\text{Log } K_{ow} \geq 2$
- Measure or estimate sediment OC
  - EqP works where  $\text{OC} = 0.2\% \text{ to } 50\%$



# Appropriate Water Quality Criteria

- Saltwater vs freshwater
- Chronic values
- Protective of organisms actually at site
  - Invertebrates
  - Warm water spp (Georgia)





# Appropriate Water Quality Criteria

- USEPA National Recommended Water Quality Criteria
- Georgia Criteria

The screenshot displays two web pages. On the left is the EPA website, showing the navigation menu and the 'National Recommended Water Quality Criteria' page. On the right is the Georgia EPD website, showing the 'Georgia Water Quality Standards' page. A yellow callout box is overlaid on the EPA page, containing the text: ***Make sure standards are not based on fish or human health!!***

**EPA Website:**  
United States Environmental Protection Agency  
LEARN THE ISSUES | SCIENCE & TECHNOLOGY | LAWS & REGULATIONS | ABOUT EPA  
Water: Current Water Quality Criteria  
You are here: Water » Science & Technology » Surface Water Quality Criteria » National Recommended Water Quality Criteria  
**National Recommended Water Quality Criteria**  
EPA's compilation of national recommended water quality criteria is a table containing recommended water quality criteria for protection of human health in surface water for approximately 150 parameters pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and tribes to use in adopting water quality standards.

**Georgia EPD Website:**  
Environmental Protection Division  
Georgia Department of Natural Resources  
EPD Home | DNR Home | Georgia Home | About EPD | EPD Offices | Contact EPD  
**Georgia Water Quality Standards**  
The overall goal of the Federal Clean Water Act is to restore and maintain the chemical, physical and biological integrity of the Nation's waters. Water quality standards are a key tool used by States to meet this goal and are a fundamental component of watershed management. Water quality standards are the foundation for numerous activities conducted by Georgia EPD including development of [Total Maximum Daily Loads \(TMDLs\)](#), issuance of National Pollutant Discharge Elimination System (NPDES) permits and assessment of State waters as part of the [305\(b\)/303\(d\) listing process](#).

**Additional Notes**

- **Appendix A**—Conversion Factors for Dissolved Metals
- **Appendix B**—Parameters for Calculating Freshwater Dissolved Metals Criteria That Are Hardness-Dependent
- **Appendix C**—Calculation of Freshwater Ammonia Criterion
- **Gold & Red Books**



# Appropriate Water Quality Criteria

- Risk Assessment Information System
- <http://rais.ornl.gov> > Tools > Eco Benchmarks

The screenshot shows the RAIS website header with a map of the United States, the title "RAIS The Risk Assessment Information System", and navigation links for Home, About, Contact, and Site Map. Below the header is a row of six photographs showing various environmental remediation or construction sites. A blue navigation bar contains the following menu items: TOOLS, TUTORIALS, GUIDANCE, PARTNERS, EPA TOOLS, FAQ, and WHAT'S NEW. Below this bar is a "TRAINING" section with a grey background. Underneath, there is a breadcrumb trail: Documents > Glossary > Support > User's List. To the right of the breadcrumb trail is a search box with the text "Search..." and a "GO!" button. At the bottom of the page, the text "Ecological Benchmark Tool" is displayed in a large blue font.



# Literature (peer reviewed or reports)

*Environmental Toxicology and Chemistry*, Vol 13, pp 157-166, 1994  
Printed in the USA Pergamon Press Ltd

0730-7268/94 \$6 00 + 00



*Environmental Toxicology and Chemistry*, Vol. 15, No. 7, pp. 1232-1241, 1996  
Printed in the USA  
0730-7268/96 \$6.00 + .00

*Arch. Environ. Contam. Toxicol.* 46, 324-335 (2004)  
DOI: 10.1007/s00244-003-2315-3

ARCHIVES OF  
**Environmental**

TO



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*Ecotoxicology*, 14, 355-380, 2005

## Comparison of Labor the Pyrethroid Insect

A. F. W. Schroer,<sup>1</sup> J. D. M. Be

<sup>1</sup> Alterra Green World Research, P.O.

<sup>2</sup> Syngenta Crop Protection AG, 4002

Received: 22 January 2003/Accepted

**Abstract.** The toxicity of the pyrethroid insecticides to freshwater invertebrates has been

## Threshold Levels for Effects of Insecticides in Freshwater Ecosystems: A Review

RENÉ P. A. VAN WIJNGAARDEN,\* THEO C. M. BROCK AND PAUL J. VAN DEN BRINK  
*Alterra, Wageningen UR, P.O. Box 47, NL-6700 AA Wageningen,  
The Netherlands*

Accepted 23 January 2004

**Abstract.** A literature review of freshwater (model) ecosystem studies with neurotoxic insecticides was performed to assess ecological threshold levels, to compare these levels with the first tier approach within European Union (EU) administration procedures, and to evaluate the ecological consequences of exceeding these thresholds. Studies published between 1980 and 2001 were reviewed. Most studies covered organophosphates and synthetic pyrethroids in lentic waters. The most sensitive taxa were representatives of crustaceans, insects and fish. Based on toxic units, threshold values were equivalent for compounds with a



# Appropriate Water Quality Criteria

- May have to develop based on toxicity test data
- Appropriate criterion
  - Exposure time
  - Reasonable protective level

The screenshot shows the ECOTOX Database website. At the top right, it says "U.S. ENVIRONMENTAL PROTECTION AGENCY". The main header is "ECOTOX Database" with a "Share" button. Below the header, there are links for "Recent Additions" and "Contact Us". A search bar is present with radio buttons for "All EPA" and "This Area" (which is selected), and a "Go" button. A breadcrumb trail reads "You are here: EPA Home » ECOTOX". On the left side, there is a navigation menu with links for "Home", "About ECOTOX", "Limitations", "Help Center", and "Frequent Questions". At the bottom, there are two large buttons: "Quick Database Query" and "Advanced Database Query", each with a colorful illustration of various animals and plants.



# Appropriate Partitioning Value

- Hazardous Substance Data Base
- <http://toxnet.nlm.nih.gov/>
- Look for soil adsorption/mobility section

The screenshot shows the HSDB website interface. At the top, there are navigation buttons: "Next Item", "Search Results", "Basic Search", "Details", "Other Files", and "Modify Search". Below these are "Download", "Limits", "Browse Index", and "Help". On the right, there is a "TOXNET Home" button and the "NATIONAL LIBRARY OF MEDICINE" logo, with the text "Item 1 of 1950".

The left sidebar contains a list of categories, with "Soil Adsorption/Mobility" selected. The main content area displays the following information for Benzene:

**BENZENE**  
CASRN: 71-43-2

c1ccccc1

*For other data, click on the Table of Contents*

**Soil Adsorption/Mobility:**  
An experimentally derived log Koc of 1.93 (Koc = 85) was obtained via reverse phase HPLC (High Performance Liquid Chromatography) with a cyanopropyl column and a mobile phase of water(1). According to a classification scheme(2), this estimated Koc value suggests that **benzene** is expected to have high mobility in soil. The sorption equilibrium for **benzene** in a soil/water mixture (ratio soil/water 0.12 kg/l) took 72 hrs(3). The Koc for **benzene** has also been experimentally determined to be 79(4).



# Appropriate Partitioning Value

- Agency for Toxic Substances & Disease Registry
- <http://www.atsdr.cdc.gov/substances/indexAZ.asp>

The screenshot shows the ATSDR website interface. At the top left is the ATSDR logo and the text "Agency for Toxic Substances & Disease Registry" next to a search box. Below this is a navigation bar with "A-Z Index" and a list of letters from A to Z, plus a hash symbol. The main heading is "Toxic Substances Portal". On the left is a green sidebar menu with the following items: "Toxic Substances Portal", "Substances List" (with a right-pointing arrow), "Substances Resources", "Substances Map", "Health Effects of Exposure to Substances and Carcinogens", "Chemical Classifications", "Community Members", "Emergency Responders", and "Medical Education and Training". To the right of the sidebar, there is a link for "Toxic Substances Portal" and a heading "Substances A-Z". Below the heading is an image of several laboratory test tubes and beakers containing liquids of various colors (green, red, blue, orange).



# Measured Organic Carbon

- “Relatively cheap” laboratory analysis (<\$40/sample?)
- More samples = better understanding of range of OC concentrations
  - May vary from location to location
  - May vary seasonally b/c leaf-fall
- 0.2% to 50% (extremes)
- 2-15% (more common)



## Calculate OC Normalized Criterion

$$SD_{(oc)} = K_{oc} \times SW \times \text{conversion}$$

$$\text{Sediment Criterion } \frac{\mu\text{g}}{\text{G}_{oc}} = K_{oc} \times \text{WQC } \frac{\mu\text{g}}{\text{L}} \times 0.001$$

- Sed Criterion in micrograms per gram organic carbon
- Koc value from literature
- Water quality criterion in micrograms per liter
- Unit conversion of 0.001



# USEPA 2008

CAS Number	Chemical	Log K <sub>OC</sub>	Conventional* ESB (µg/g <sub>OC</sub> )	
			Freshwater	Marine
58899	Gamma-BHC, Lindane	3.67	0.37	-
92524	Biphenyl	3.89	110	110
101553	4-Bromophenyl phenyl ether	4.92	120	120
85687	Butyl benzyl phthalate	4.76	1100	-
108907	Chlorobenzene	2.81	41	41
333415	Diazinon	3.64	0.74	3.6



Convert to  $\mu\text{g}/\text{kg}$  sediment

$$SD_{(\text{kg})} = SD_{(\text{oc})} \times \text{OC}$$

$$\text{Sediment Criterion } \frac{\mu\text{g}}{\text{KG sediment}} = \text{Criterion } \frac{\mu\text{g}}{\text{G}_{\text{oc}}} \times \frac{\text{G Organic Carbon}}{\text{KG Sediment}}$$

- Multiply criterion by OC concentration
- Results in sediment criterion in usable units
- Shorthand trick... calculate for 1% OC and multiply it by actual % OC



**Multiply by 15**

**Multiply by 5**

1% & 5% values from USEPA 2008 Table 3-4	Dry Weight Sediment Concentration (mg/kg sd)			USEPA Region 4 or 5 Screening Criteria (mg/kg sd)
Chemical Name	at 1% TOC	at 5% TOC	at 15% TOC	
Benzene	0.16	0.8	2.4	0.142 (R5)
Chlorobenzene	0.41	2.1	6.15	0.291 (R5)
Lindane	0.0037	0.019	0.055	0.0033 (R4)
Dibenzofuran	0.37	1.9	5.55	0.449 (R5)

Benchmark = Toxic Unit of 1





# Important Safety Tips!

- For chemicals with  $K_{oc} \geq 2$
- For OC 0.2% to 50%
- Nonstandard OC may alter partitioning
  - (rubber, animal or wood processing wastes, relatively undegraded woody debris or plant matter, black carbon, soot, coal, ashes)



# Important Safety Tips!

- For direct toxicity to sediment invertebrates, not food-chain
- Non-equilibrium
  - High sd erosion rates
  - High concentrations
  - Undissolved particles in sd

