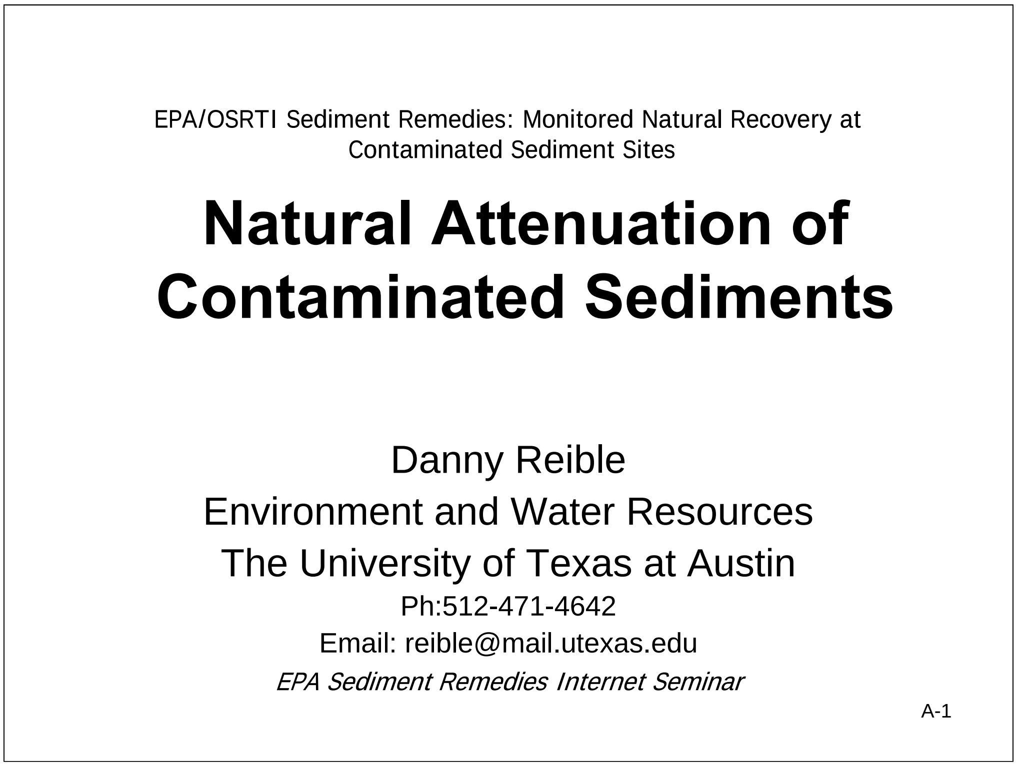


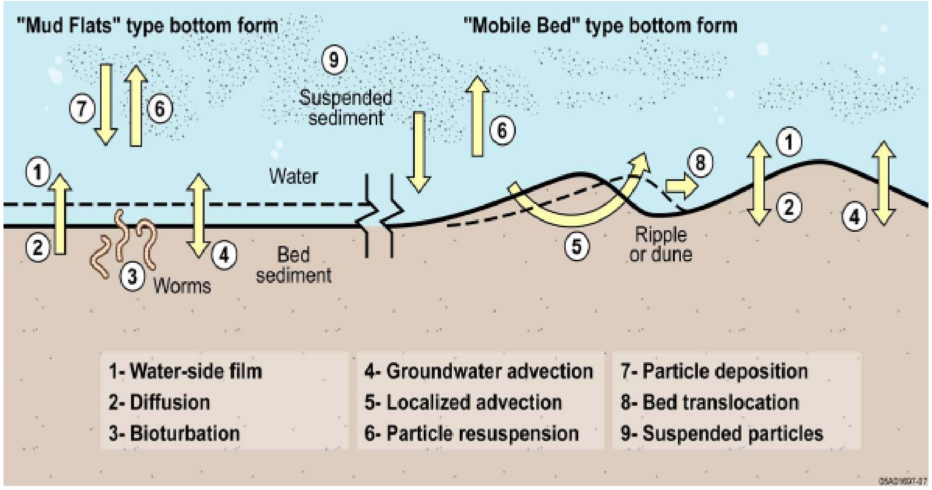
EPA/OSRTI Sediment Remedies: Monitored Natural Recovery at
Contaminated Sediment Sites

Natural Attenuation of Contaminated Sediments

Danny Reible
Environment and Water Resources
The University of Texas at Austin
Ph:512-471-4642
Email: reible@mail.utexas.edu

EPA Sediment Remedies Internet Seminar

Selected Sediment Processes



	Environmental Characteristics	**Key Fate and Transport Processes**
Lacustrine	Low energy environment Generally depositional environment Groundwater interaction decreasing away from shore Organic matter decreasing with distance from shore Often fine-grained sediment	Sediment deposition Water-side mass transfer limitations Groundwater advection in near-shore area Bioturbation (especially in near-shore area) Diffusion in quiescent settings Metal sorption Aerobic and anaerobic biotransformation Biotransformation of organic matter (e.g., gas formation)
Riverine	Low to high energy environment Depositional or erosional environment Potential for significant groundwater interaction Significant variability in flow and sediment characteristics within and between rivers	Local and generalized groundwater advection Sediment deposition and resuspension Aerobic biotransformation processes in surficial sediments (potentially anaerobic at depth) Bioturbation

	Environmental Characteristics	Key Fate and Transport Processes
Estuarine	Generally low energy environment Generally depositional environment Generally fine-grained sediment Grading to coarse sediment at ocean boundary	Bioturbation Sediment deposition Water-side mass transfer limitations Aerobic and anaerobic biotransformation of contaminants Biotransformation of organic matter (e.g., gas formation)
Coastal Marine	Relatively high energy environment, decreasing with depth and distance from shore Often coarse sediments	Bioturbation Sediment erosion and deposition Localized advection processes

Table C-2
Summary of Characteristic Times of Sediment Fate and Transport Processes

Process	Characteristic Time Relationship	Typical Range of Key Parameter Values	Illustrative Value of Characteristic Time[1]
Diffusion	$\tau_{diff} = \frac{4}{\pi^2} \frac{H^2 R_f}{D_{eff}}$	$R_f > 1{,}000$ (Hydrophobicorganics) $D_{eff} \sim 10^{-6}$ cm^2/s	1,280 years
Advection	$\tau_{adv} = \frac{H\,R_f}{v}$	Groundwater velocity v, widely variable	100 years
Sediment Erosion	$\tau_{ero} = \frac{H}{U}$	Bed erosion rate, U, widely variable	10 years
Bioturbation	$\tau_{bio} = \frac{4}{\pi^2} \frac{H^2}{D_{bio}}$	0.3 cm^2/yr$<D_{bio}<$30 cm^2/yr	13 years
Reaction	$\tau_{fate} = \frac{1}{k_{rxn}}$	Reaction rate, k_{rxn}, widely variable	100 years

Assumes a 10m thick surface layer contaminated with a hydrophobic organic compound with an effective retardation factor of 1000 (e.g. a mid range PA H such as pyrene), a ground water up welling velocity of 1 m/yr, a bed erosion rate of 1 cm/yr, an effective bioturbation diffusion coefficient of 3 cm^2/yr and a degradation rate of 0.01 yr^{-1}

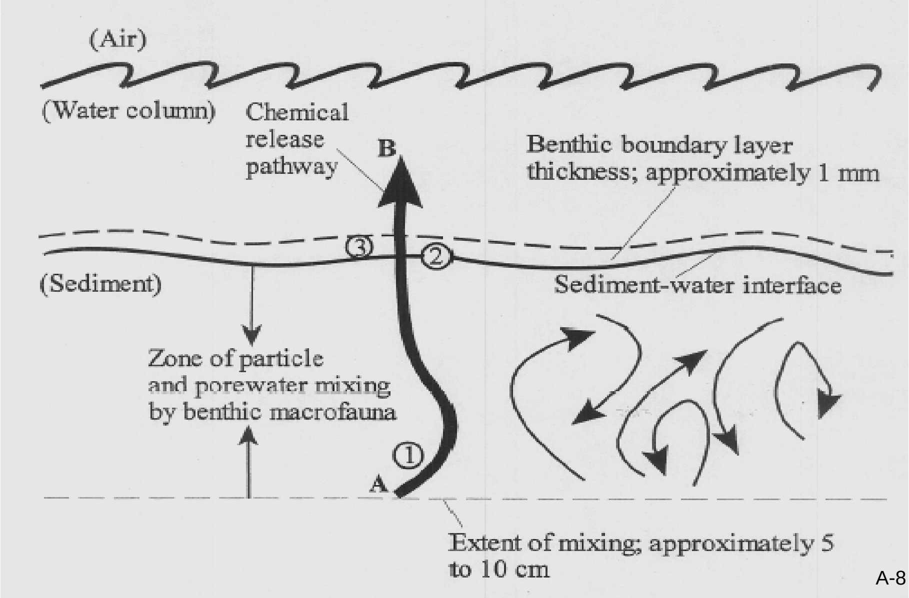
Exposure and Risk in Overlying Water

- Direct flux to overlying water
  - Erosion and resuspension of contaminated sediment where applicable
  - Bioturbation moderated by partitioning and mass transfer resistances at sediment-water interface
- Accumulation in benthic community and food-chain transfer
  - Limited to depth of bioturbation
  - Limited by availability of contaminants to organisms

Bioturbation

- Normal life cycle activities of benthic organisms leading to sediment mixing and transport
  - Controls depth of sediments leading to exposure
    - Typically 5-15 cm
    - Controls access to contaminants
  - Controls rate of sediment reworking and porewater release
    - 0.3-30 cm/yr average sediment reworking rate (solid basis)
    - >100 cm/yr average porewater exchange rate (fluid basis)
- Dominated by deposit feeders that ingest sediment
  - Freshwater oligochaetes
    - Densities up to 100,000 worms/m2 or more
    - Organisms may process 10-20 times their wt/day

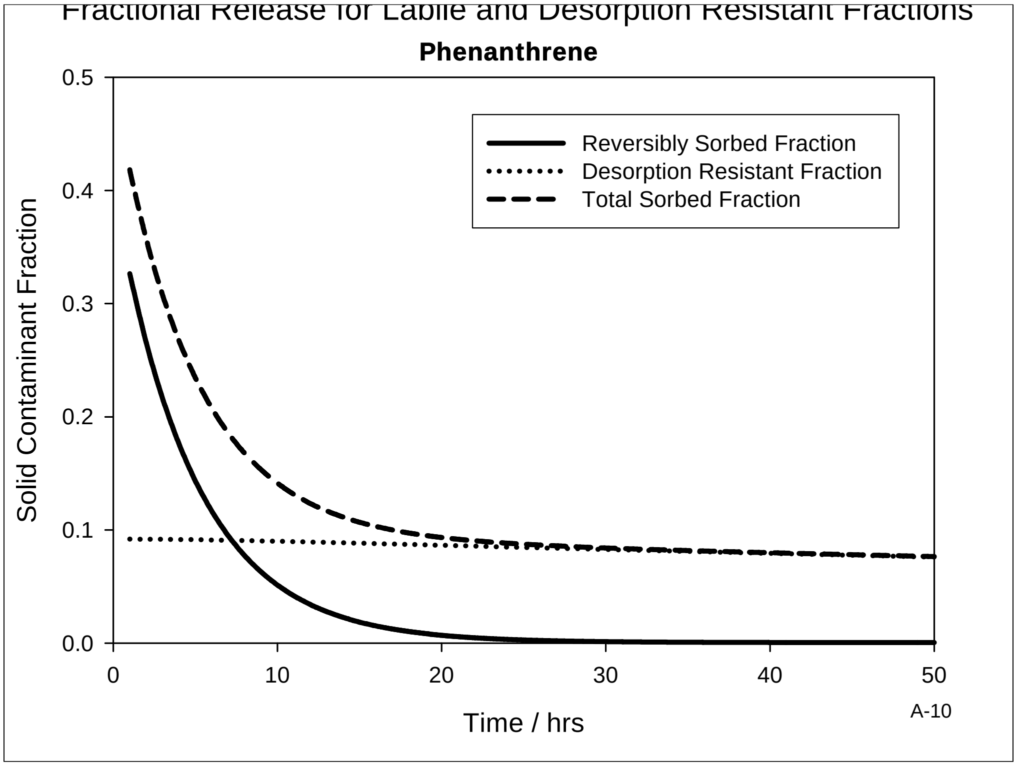
The Bioturbation/Soluble Release Process



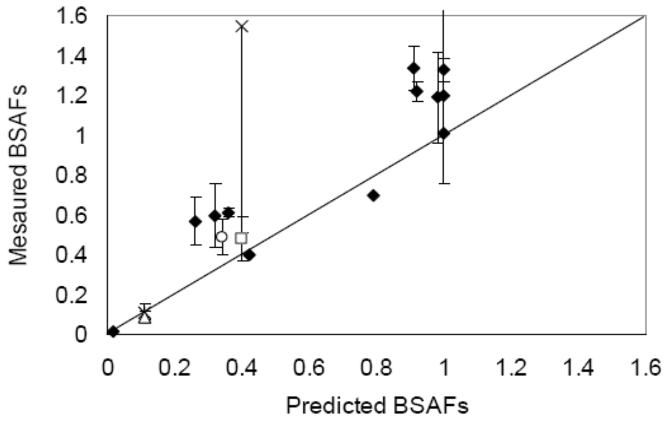
A-8

Variety of processes may complicate this simple picture

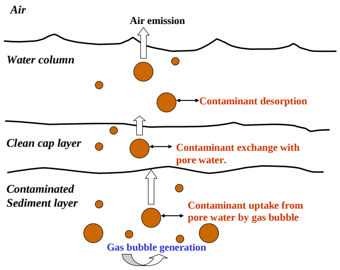
- Limited bioavailability
  - e.g. does pore water better correlate with availability than bulk sediment concentration?
- Presence of multiple contaminant phases
  - e.g. gas or non aqueous phase liquids
- Fate processes that affect exposure
  - e.g.limited mercury methylation
- Presence of other sources that limit recovery
  - e.g. Slowing passive recovery and negating active recovery


Fractional Release for Labile and Desorption Resistant Fractions
Phenanthrene
Solid Contaminant Fraction
0.0
0.1
0.2
0.3
0.4
0.5
Time / hrs
0
10
20
30
40
50
Reversibly Sorbed Fraction
Desorption Resistant Fraction
Total Sorbed Fraction
A-10

BSAFs predicted by porewater concentrations (field and lab sediment)



Contaminant Release via Gas Ebullition



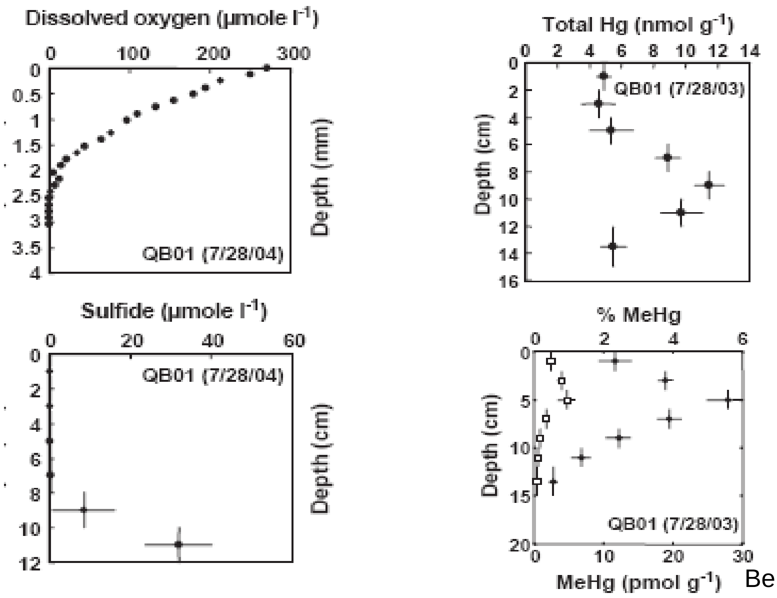
q_v Gas Flux (L/m^2·day)	N_A Flux PHE mg/m^2·hr	k_{eff} ($N_A/\rho_b W_s$) cm/yr
1	**0.00030**	**0.0033**

Relatively low – *unless* NAPL entrained in gas bubbling to surface

Compares to
~ 1 cm/yr Bioturbation

A-12

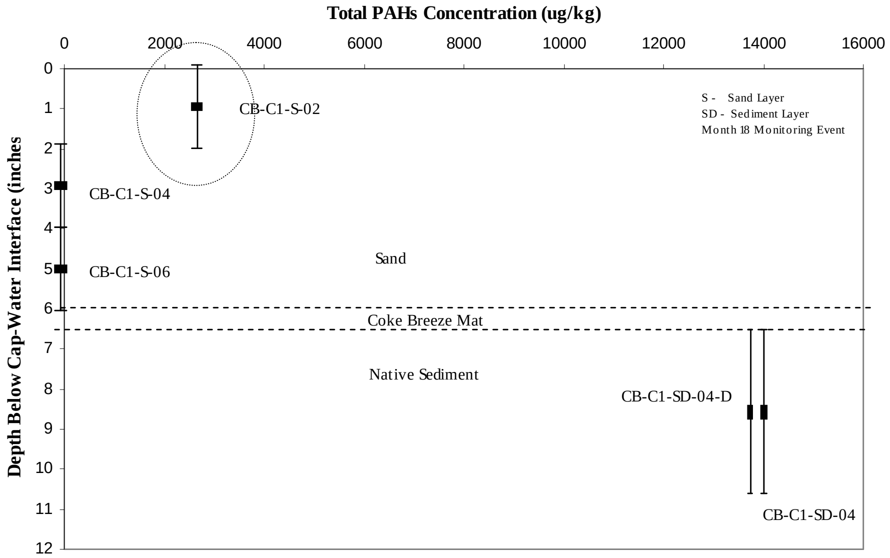
Thin zone of mercury methylation



A-13

Benoit et al.

Recontamination of Surface Anacostia River



MNR Definitions

Monitored Natural Recovery (MNR) involves *leaving contaminated sediments in place* and allowing ongoing aquatic, sedimentary, and biological processes to reduce the bioavailability of the contaminants in order to *protect receptors*

[MNR] must be the result of a deliberate, thoughtful decision-making process following careful site assessment and characterization

NRC, 1997. *Contaminated Sediments in Ports and Waterways*

MNR…uses known, ongoing, naturally occurring processes to contain, destroy, or otherwise *reduce the bioavailability or toxicity of contaminants* in sediment.

MNR…includes…monitoring to assess whether risk is being reduced as expected.

USEPA, 2005. *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites*

2005 *EPA Guidance*

(Highlight 4-1: Hierarchy of Natural Processes)

A. Contaminant **transformation** to a less toxic form (biological or abiotic transformation)

B. Reduced contaminant **mobility/bioavailability** (sorption or binding processes)

C. Reduced **exposure** at the **sediment surface** (burial, in-place mixing with cleaner sediment)

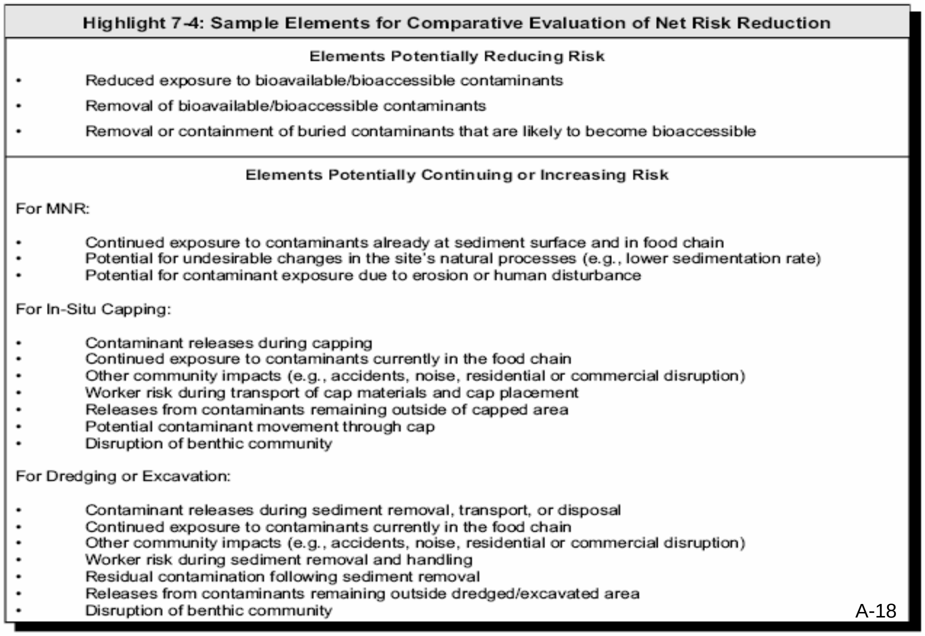
D. Contaminant release and off-site transport (particle dispersion, diffusive/advective transport)

Remedy Selection Considerations

- The Guidance encourages project managers to use the concept of comparing net risk reduction between alternatives a part of the remedy selection process.
- Highlight 7-4 covers elements of comparative net risk for MNR, capping and dredging

(Sediment Guidance, p. 7-13)

Highlight Box 7-4



Highlight 7-4: Sample Elements for Comparative Evaluation of Net Risk Reduction

Elements Potentially Reducing Risk

- Reduced exposure to bioavailable/bioaccessible contaminants
- Removal of bioavailable/bioaccessible contaminants
- Removal or containment of buried contaminants that are likely to become bioaccessible

Elements Potentially Continuing or Increasing Risk

For MNR:

- Continued exposure to contaminants already at sediment surface and in food chain
- Potential for undesirable changes in the site's natural processes (e.g., lower sedimentation rate)
- Potential for contaminant exposure due to erosion or human disturbance

For In-Situ Capping:

- Contaminant releases during capping
- Continued exposure to contaminants currently in the food chain
- Other community impacts (e.g., accidents, noise, residential or commercial disruption)
- Worker risk during transport of cap materials and cap placement
- Releases from contaminants remaining outside of capped area
- Potential contaminant movement through cap
- Disruption of benthic community

For Dredging or Excavation:

- Contaminant releases during sediment removal, transport, or disposal
- Continued exposure to contaminants currently in the food chain
- Other community impacts (e.g., accidents, noise, residential or commercial disruption)
- Worker risk during sediment removal and handling
- Residual contamination following sediment removal
- Releases from contaminants remaining outside dredged/excavated area
- Disruption of benthic community

EPA/OSRTI Sediment Remedies: Monitored Natural Recovery at
Contaminated Sediment Sites

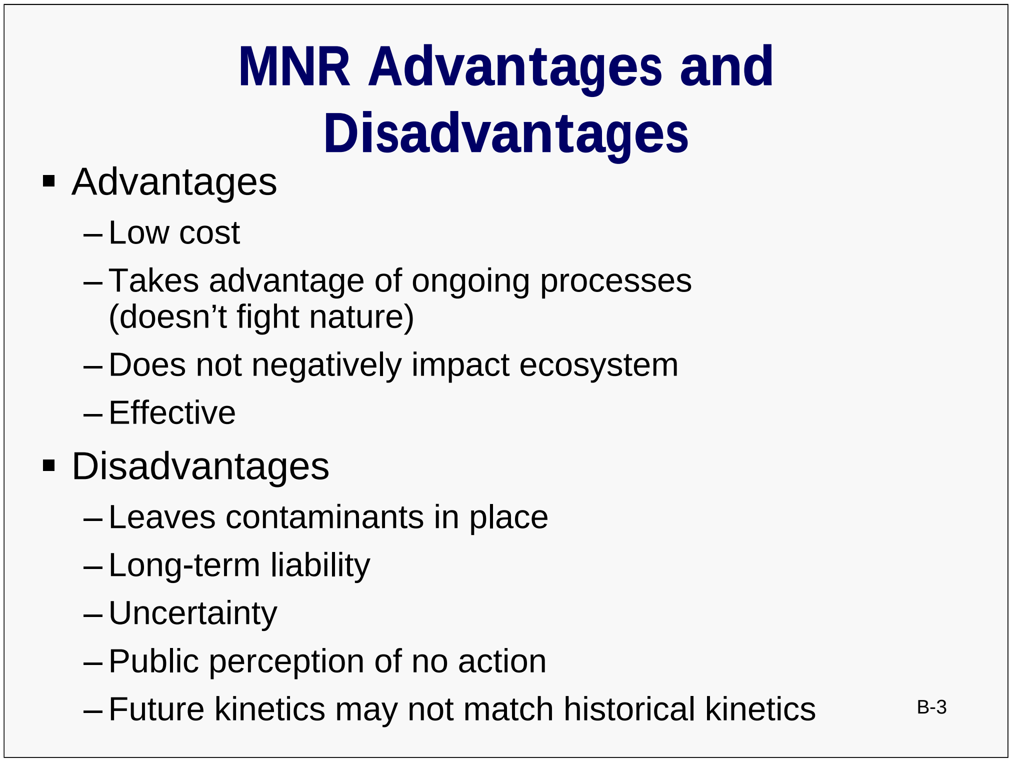
Monitored Natural Recovery at Contaminated Sediment Sites

Victor S. Magar, PhD, PE
ENVIRON - Chicago, IL
vmagar@environcorp.com
(312) 853-9430

Training Outline

Purpose of this Presentation:
Explore the primary lines of evidence supporting an MNR investigation, and how natural processes can facilitate sediment remediation

1. The role of natural recovery in the environment
2. MNR definitions
3. EPA 2005 *Sediment Guidance* Summary
4. Identify and describe MNR lines of evidence
5. Integrating MNR into remedy decision making



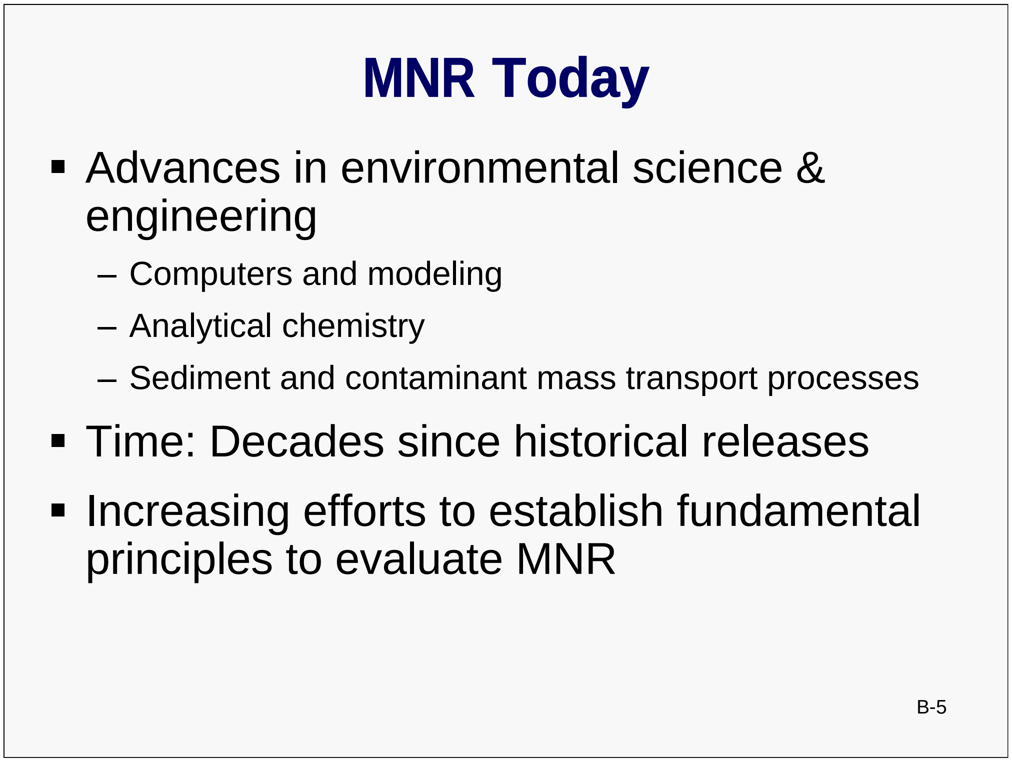
MNR Advantages and Disadvantages

- Advantages
  - Low cost
  - Takes advantage of ongoing processes (doesn’t fight nature)
  - Does not negatively impact ecosystem
  - Effective
- Disadvantages
  - Leaves contaminants in place
  - Long-term liability
  - Uncertainty
  - Public perception of no action
  - Future kinetics may not match historical kinetics

Suggest this could be initial slide in the presentation

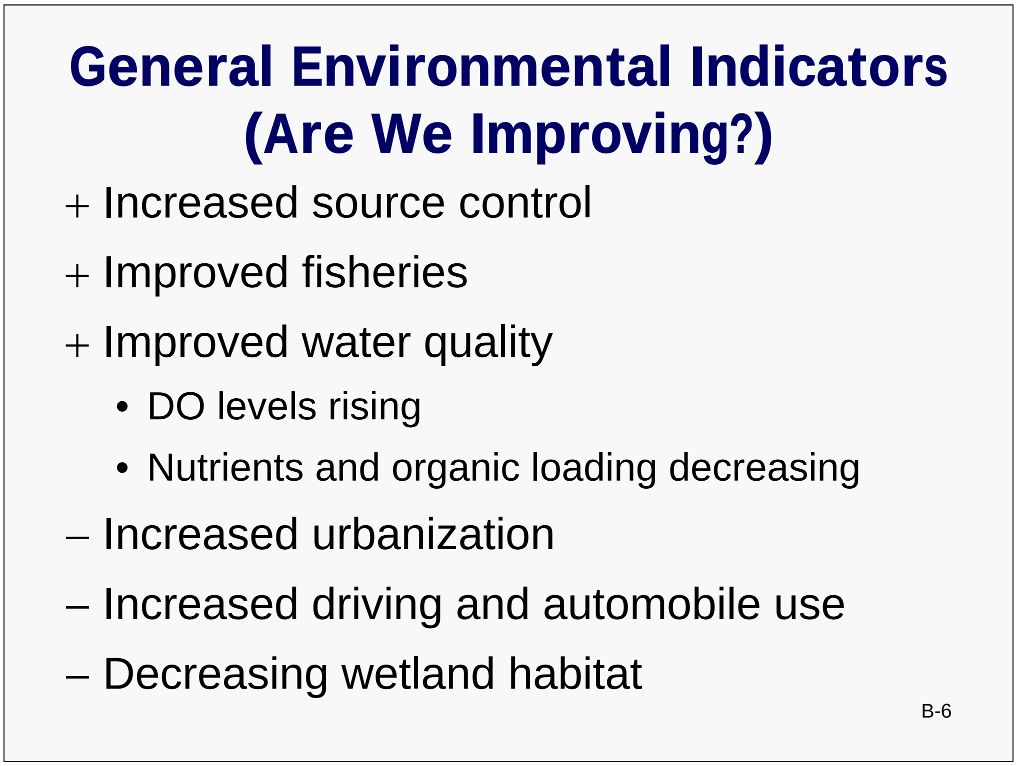
Example Sites that Identified and Selected Natural Recovery in their RODs

- Kepone, James River (VA)
  - Active remediation estimated at $3 to $10 billion
  - Active remediation would disturb existing habitat
  - Sediments likely to be buried, or diluted by flushing and mixing
- Lead, Interstate Lead Company Superfund site (AL),1995 ROD
  - Historical trends indicated a general decline in sediment lead concentrations,
  - No evidence of damage to existing ecosystem
  - Active remediation would damage existing ecosystem
  - Natural recovery would result in minimal environmental disturbance
- PCBs, Lake Hartwell Superfund site (SC), 1994 ROD
  - Active remediation technically impracticable or too costly
  - EPA and public agreed that fishing advisories could adequately reduce risk
  - Source control was implemented at the former Sangamo-Weston plant
  - 1-D (HEC-6) model predicted recovery to 1 mg/kg within a reasonable time



MNR Today

- Advances in environmental science & engineering
  - Computers and modeling
  - Analytical chemistry
  - Sediment and contaminant mass transport processes
- Time: Decades since historical releases
- Increasing efforts to establish fundamental principles to evaluate MNR



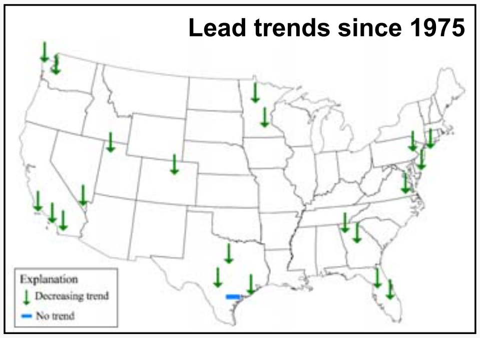
General Environmental Indicators (Are We Improving?)

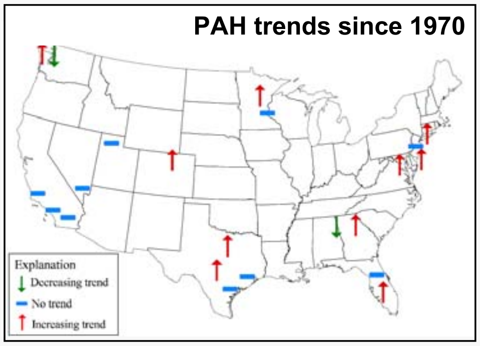
+ Increased source control
+ Improved fisheries
+ Improved water quality
  - DO levels rising
  - Nutrients and organic loading decreasing

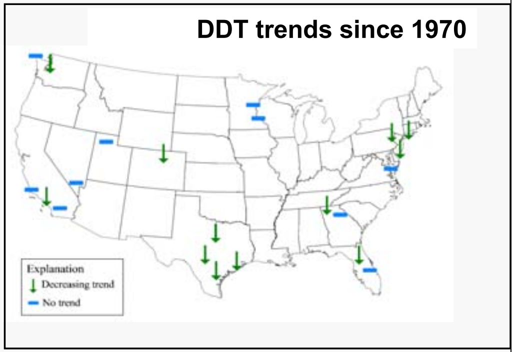
– Increased urbanization
– Increased driving and automobile use
– Decreasing wetland habitat

B-6

Impacts of Source Control: Sediment Trends in the US


Lead trends since 1975

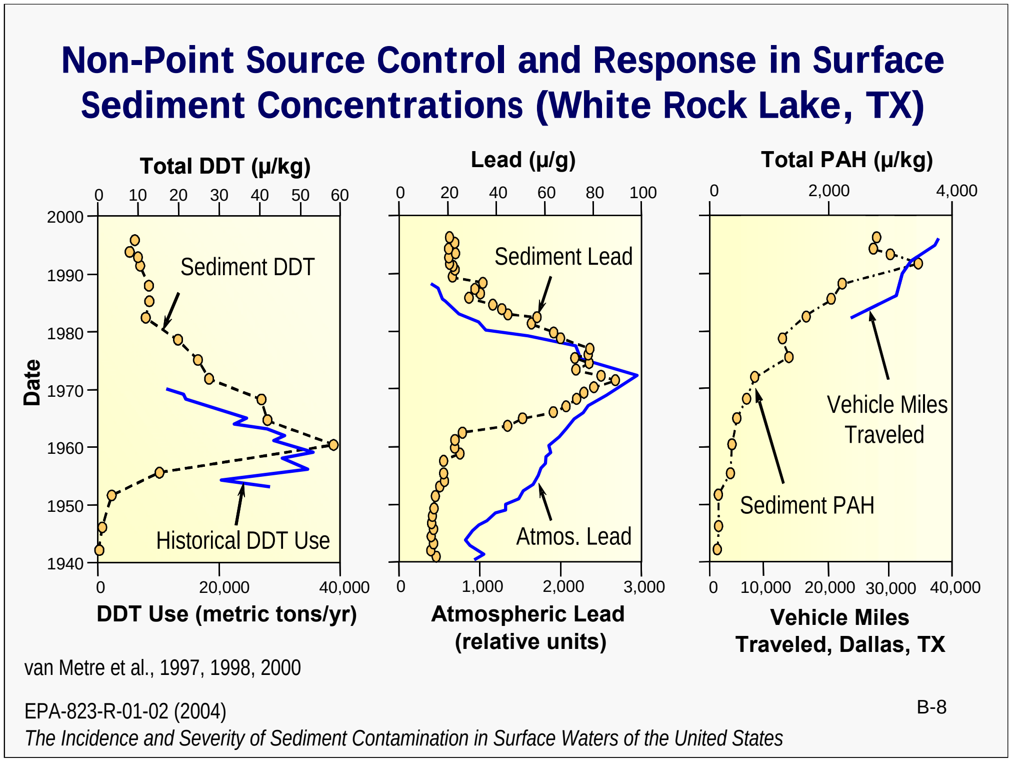

PAH trends since 1970


DDT trends since 1970

van Metre et al., 1997, 1998, 2000

EPA-823-R-01-02 (2004)
The Incidence and Severity of Sediment Contamination in Surface Waters of the United States

B-7



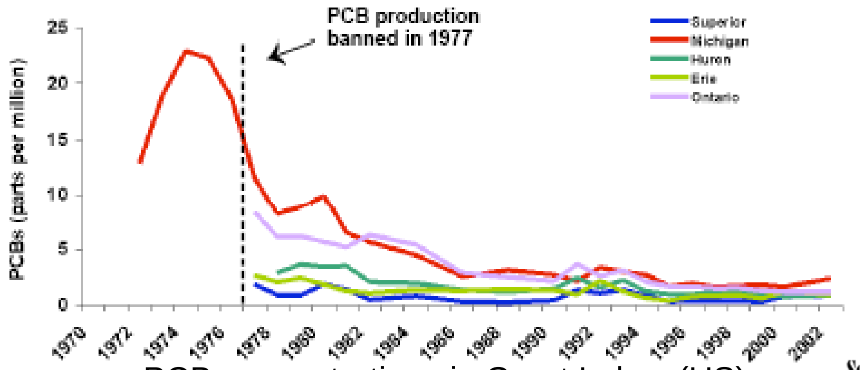
Non-Point Source Control and Response in Surface Sediment Concentrations (White Rock Lake, TX)

van Metre et al., 1997, 1998, 2000

EPA-823-R-01-02 (2004)
The Incidence and Severity of Sediment Contamination in Surface Waters of the United States

B-8

Source Control and Natural Recovery Can Contribute to Ecological Restoration



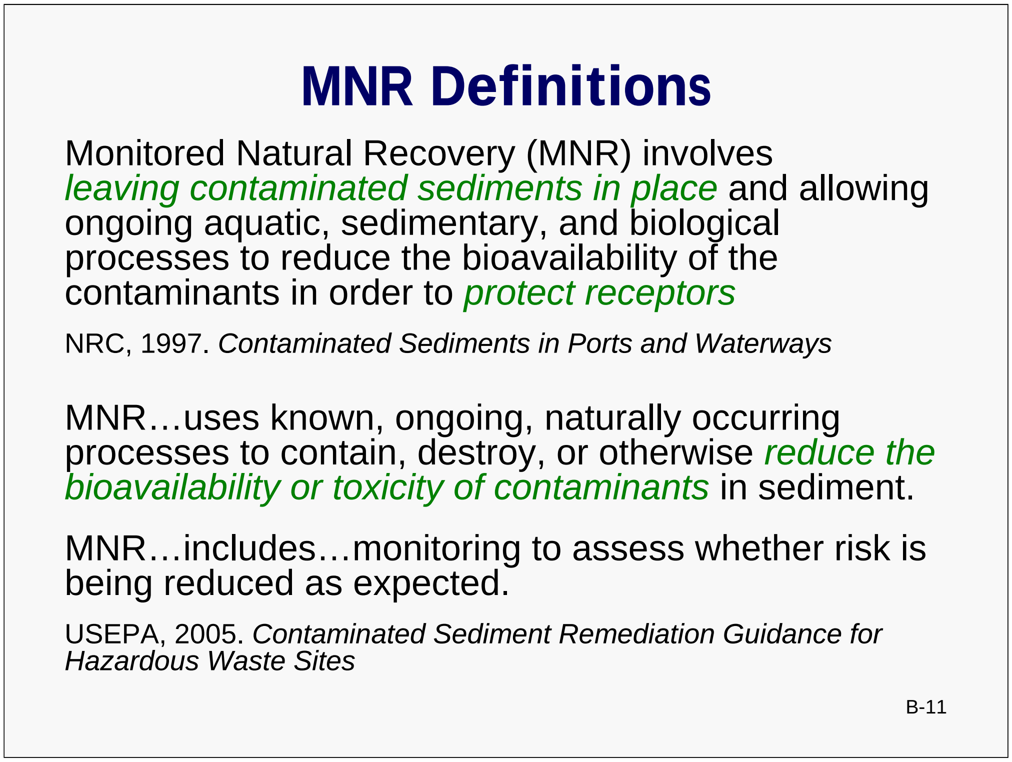
PCB concentrations in Great Lakes (US) open-water top-predator fish

B-9

http://www.iisgcp.org/products/iisg0520.pdf#search=%22%22legacy%20contaminants%22%22

Training Outline

1. The role of natural recovery in the environment
2. MNR definitions
3. EPA 2005 *Sediment Guidance* Summary
4. Identify and describe MNR lines of evidence
5. Integrating MNR into remedy decision making



MNR Definitions

Monitored Natural Recovery (MNR) involves *leaving contaminated sediments in place* and allowing ongoing aquatic, sedimentary, and biological processes to reduce the bioavailability of the contaminants in order to *protect receptors*

NRC, 1997. *Contaminated Sediments in Ports and Waterways*

MNR…uses known, ongoing, naturally occurring processes to contain, destroy, or otherwise *reduce the bioavailability or toxicity of contaminants* in sediment.

MNR…includes…monitoring to assess whether risk is being reduced as expected.

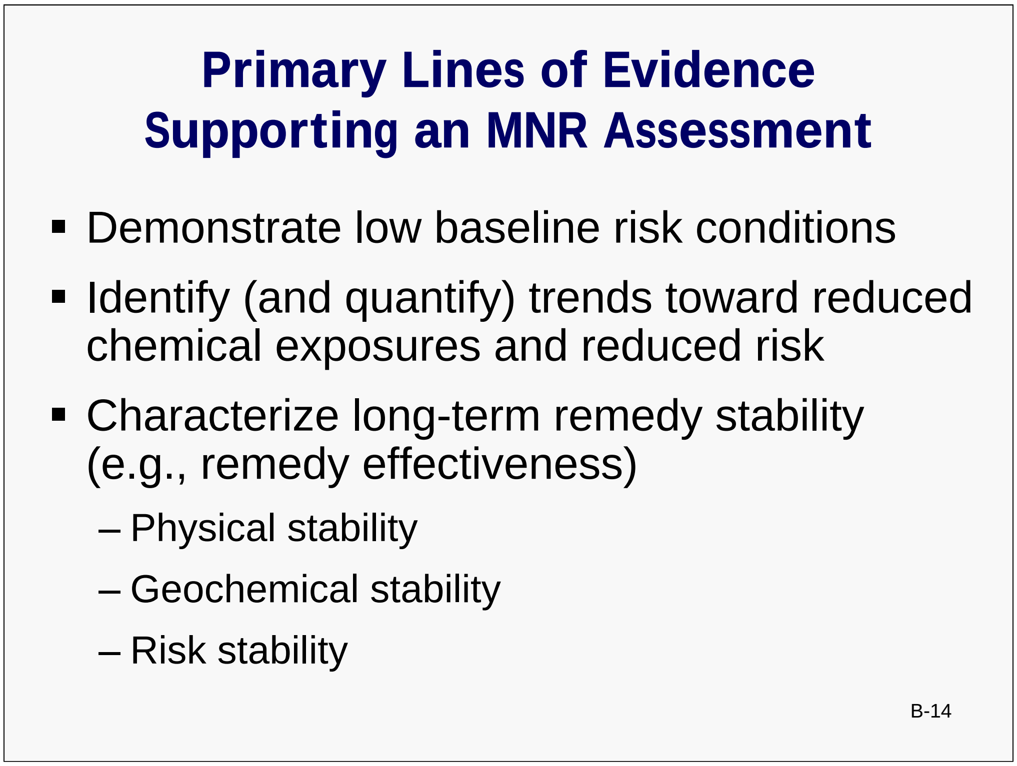
USEPA, 2005. *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites*

2005 *EPA Guidance*

- No presumed remedy: Consider all sediment management options (MNR, Capping, and Dredging) on equal footing (§ 3.1 and 3-16)
- Implement source control (§2.6 and 3.1)
- Include watershed considerations (§ 2.5)
- Comparative Net Risk: Use risk-management principles during remedy selection (§ 7.1 and 7.4)
- Include comprehensive monitoring before and after remedy implementation (Chapter 8)
- Establish the (reasonable) time to achieve risk reduction (4-12)
- MNR can be combined with other remedies (4-12)
- Additional resource materials being developed
  - MNR Technical Resource Document (EPA ORD, with support by ENVIRON and Battelle)
  - DoD MNR Guidance (2007): (ESTCP, with support by EPA, Navy, USACE, and ENVIRON)

2005 *EPA Guidance*

- No presumed remedy
  - “There should not be necessarily a presumption that removal of contaminated sediments from a water body will be necessarily more effective or permanent than capping or MNR.” (3-16)
  - “Likewise, without sufficient evaluation there should not be a presumption that capping or MNR will be effective or permanent.”(3-16)
- Combine MNR with source control and other remedies
  - At large, complex sites, PM “should consider a combination of sediment approaches…to manage the risk.” (3-2)
  - Select “site-specific, project-specific, and sediment-specific risk management approaches that will achieve risk-based goals.” (7-1)
- Remedy effectiveness and permanence
  - “[MNR is] capable of reaching acceptable levels of…effectiveness and permanence.” (3-15)
  - “…deeper contaminated sediment that is not currently bioavailable or bioaccessible, and that analyses have shown to be stable to a reasonable degree, do not necessarily contribute to site risks.” (7-3)



Primary Lines of Evidence Supporting an MNR Assessment

- Demonstrate low baseline risk conditions
- Identify (and quantify) trends toward reduced chemical exposures and reduced risk
- Characterize long-term remedy stability (e.g., remedy effectiveness)
  - Physical stability
  - Geochemical stability
  - Risk stability

2005 *EPA Guidance*

(Highlight 4-1: Hierarchy of Natural Processes)

A. Contaminant **transformation** to a less toxic form (biological or abiotic transformation)

B. Reduced contaminant **mobility/bioavailability** (sorption or binding processes)

C. Reduced **exposure** at the **sediment surface** (burial, in-place mixing with cleaner sediment)

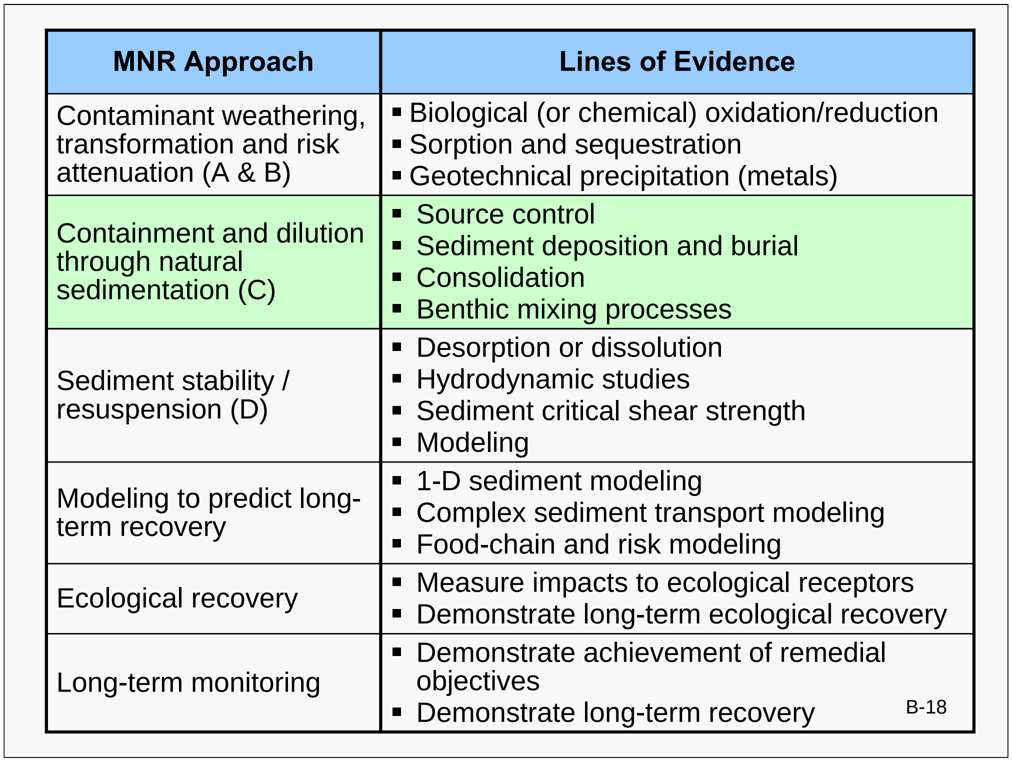
D. Contaminant release and off-site transport (particle dispersion, diffusive/advective transport)

Training Outline

1. The role of natural recovery in the environment
2. MNR definitions
3. EPA 2005 *Sediment Guidance* Summary
4. Identify and describe MNR lines of evidence
5. Integrating MNR into remedy decision making

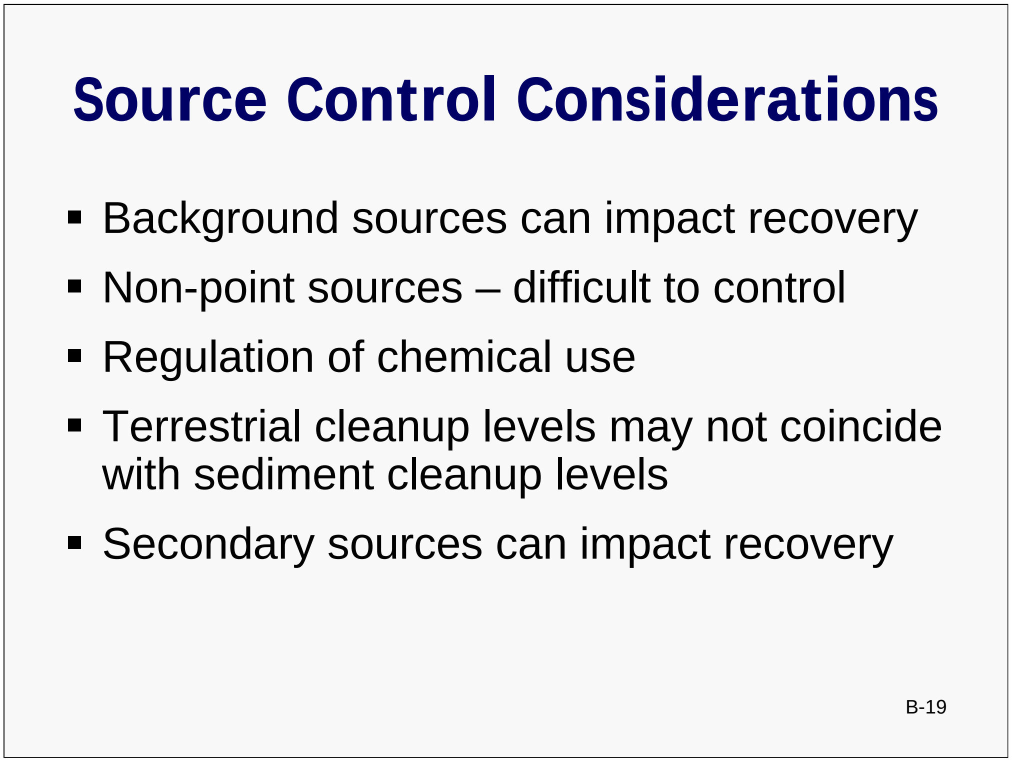
MNR Begins with the Conceptual Site Model

- A CSM is a characterization of the key overall dynamics of the site (e.g., sources, sinks, contaminant fate and transport, exposure pathways and receptors), and provides the basis for developing a remedial strategy (*EPA Guidance, § 2.2*)
- The CSM is particularly important in evaluating MNR’s potential effectiveness because it results in an understanding of the basis/drivers of risk at the site



MNR Approach	Lines of Evidence
Contaminant weathering, transformation and risk attenuation (A & B)	▪ Biological (or chemical) oxidation/reduction ▪ Sorption and sequestration ▪ Geotechnical precipitation (metals)
Containment and dilution through natural sedimentation (C)	▪ Source control ▪ Sediment deposition and burial ▪ Consolidation ▪ Benthic mixing processes
Sediment stability / resuspension (D)	▪ Desorption or dissolution ▪ Hydrodynamic studies ▪ Sediment critical shear strength ▪ Modeling
Modeling to predict long-term recovery	▪ 1-D sediment modeling ▪ Complex sediment transport modeling ▪ Food-chain and risk modeling
Ecological recovery	▪ Measure impacts to ecological receptors ▪ Demonstrate long-term ecological recovery
Long-term monitoring	▪ Demonstrate achievement of remedial objectives ▪ Demonstrate long-term recovery

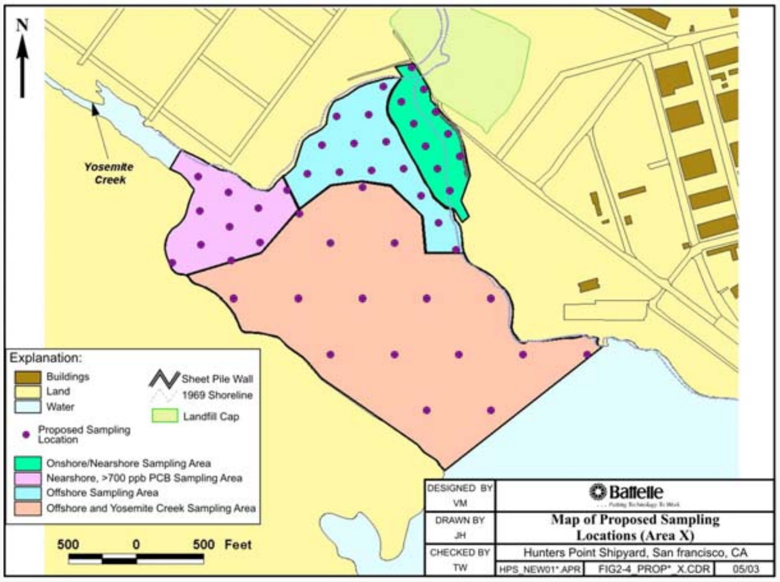
B-18



Source Control Considerations

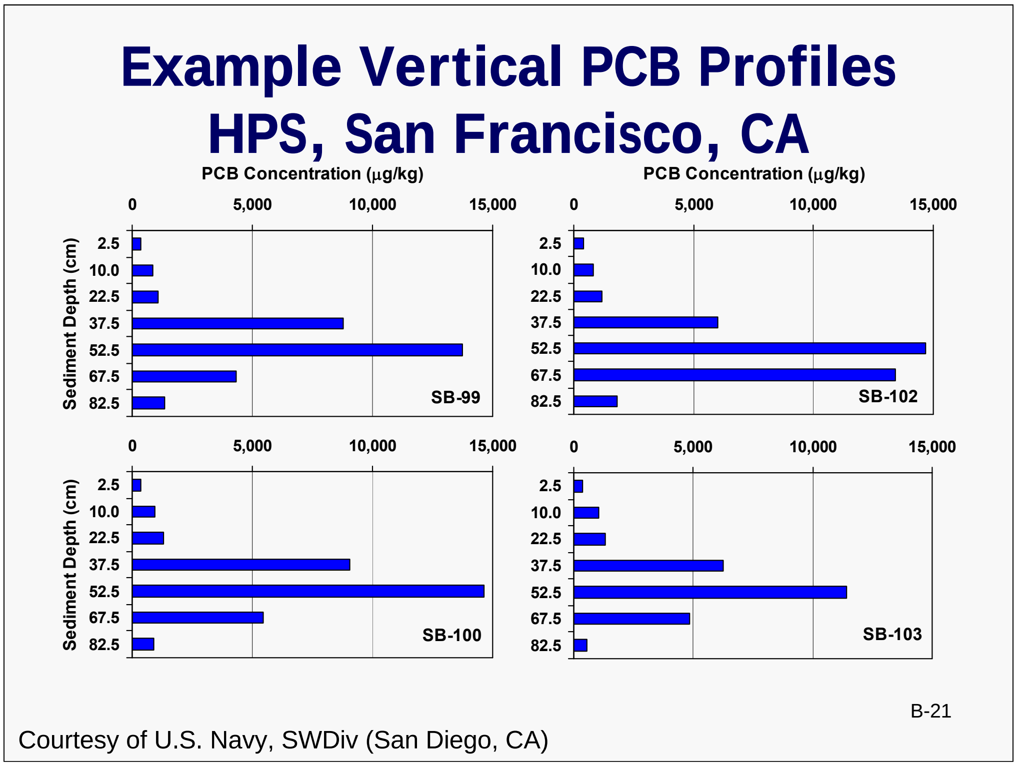
- Background sources can impact recovery
- Non-point sources – difficult to control
- Regulation of chemical use
- Terrestrial cleanup levels may not coincide with sediment cleanup levels
- Secondary sources can impact recovery

Navy Hunters Point Shipyard (HPS) Sediment Sampling Locations, San Francisco, CA



B-20

Courtesy of U.S. Navy, SWDiv (San Diego, CA)

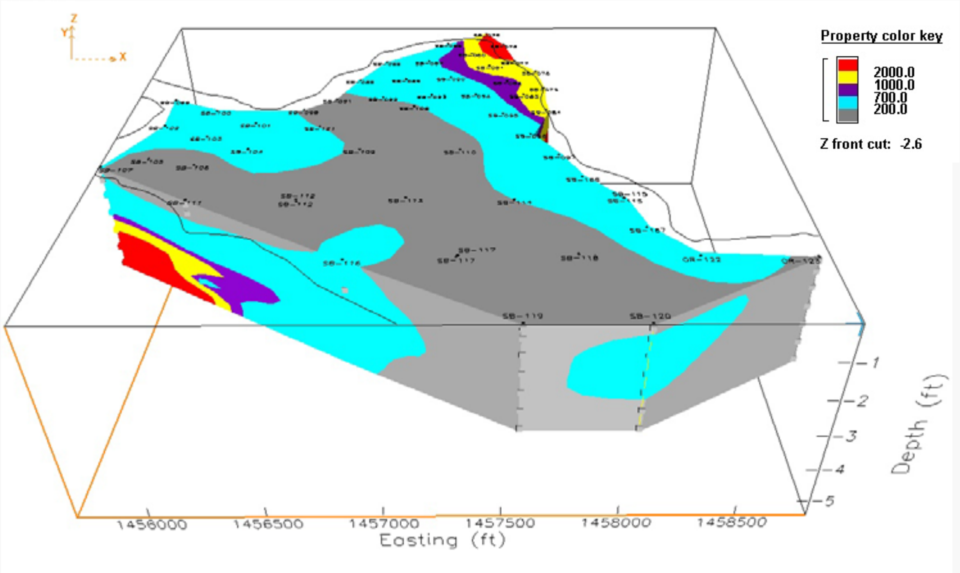


Example Vertical PCB Profiles HPS, San Francisco, CA

B-21

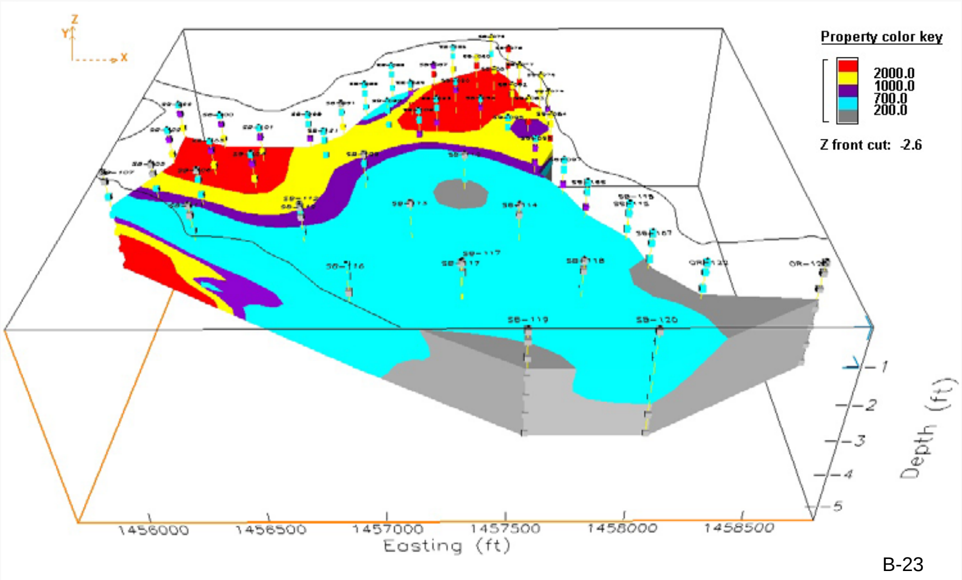
Courtesy of U.S. Navy, SWDiv (San Diego, CA)

Surface Elevation PCB (μg/kg)



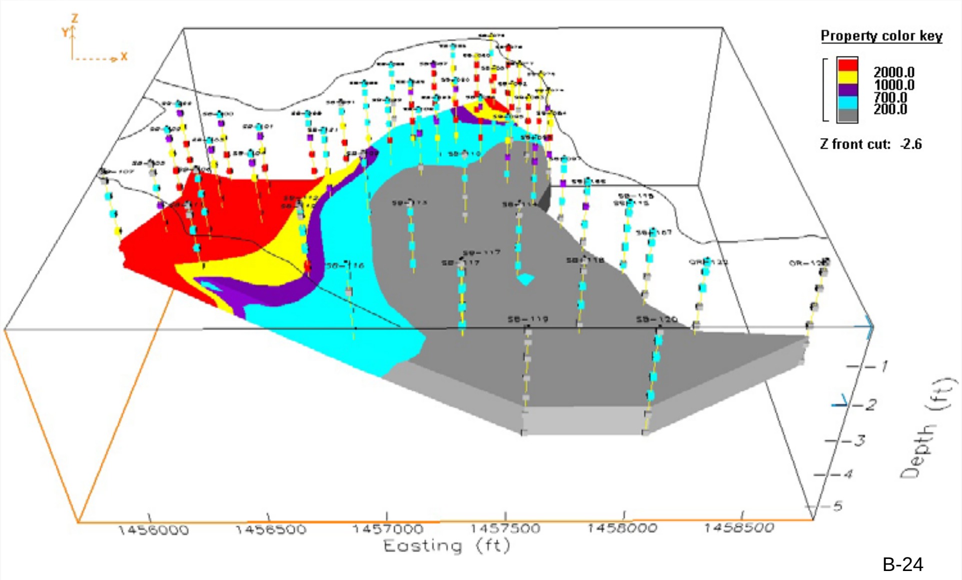
Courtesy of U.S. Navy, SWDiv (San Diego, CA)

PCB (µg/kg) at 1-ft Depth

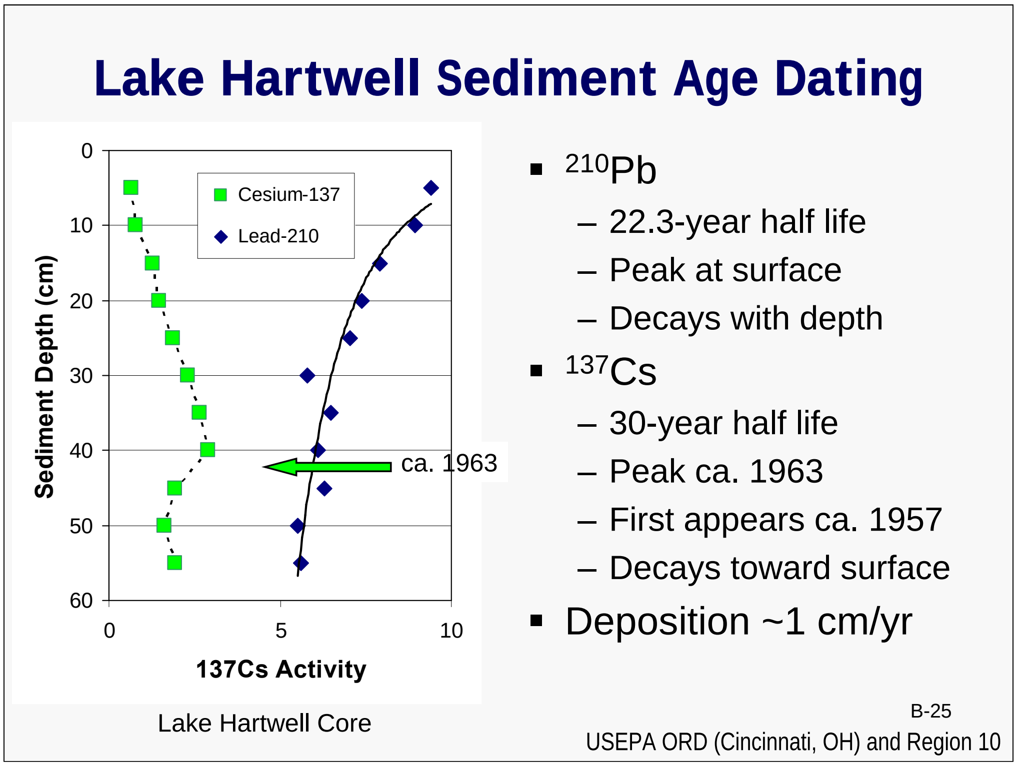


Courtesy of U.S. Navy, SWDiv (San Diego, CA)

PCB (μg/kg) at 2-ft Depth



Courtesy of U.S. Navy, SWDiv (San Diego, CA)



Lake Hartwell Sediment Age Dating

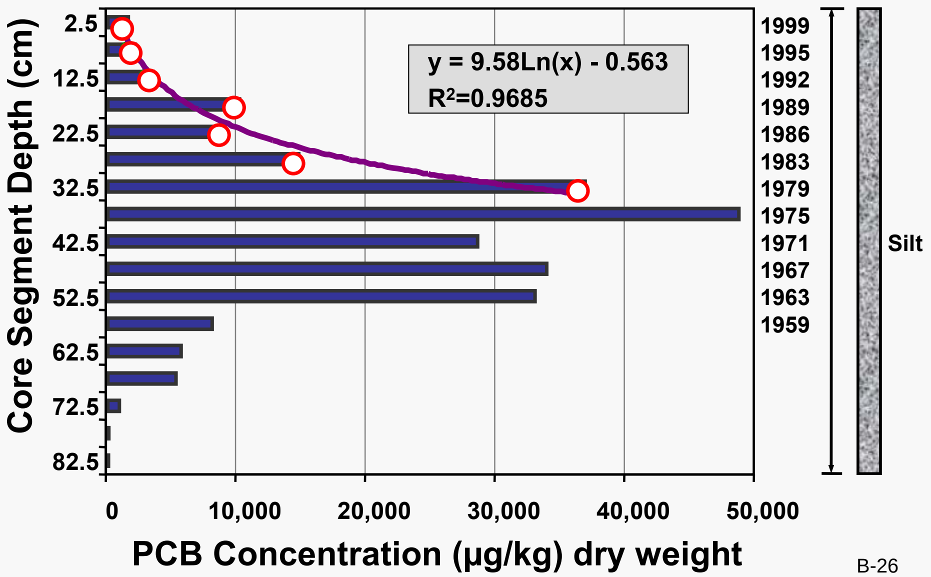
Lake Hartwell Core

- ^{210}Pb
  - – 22.3-year half life
  - – Peak at surface
  - – Decays with depth
- ^{137}Cs
  - – 30-year half life
  - – Peak ca. 1963
  - – First appears ca. 1957
  - – Decays toward surface
- Deposition ~1 cm/yr

B-25

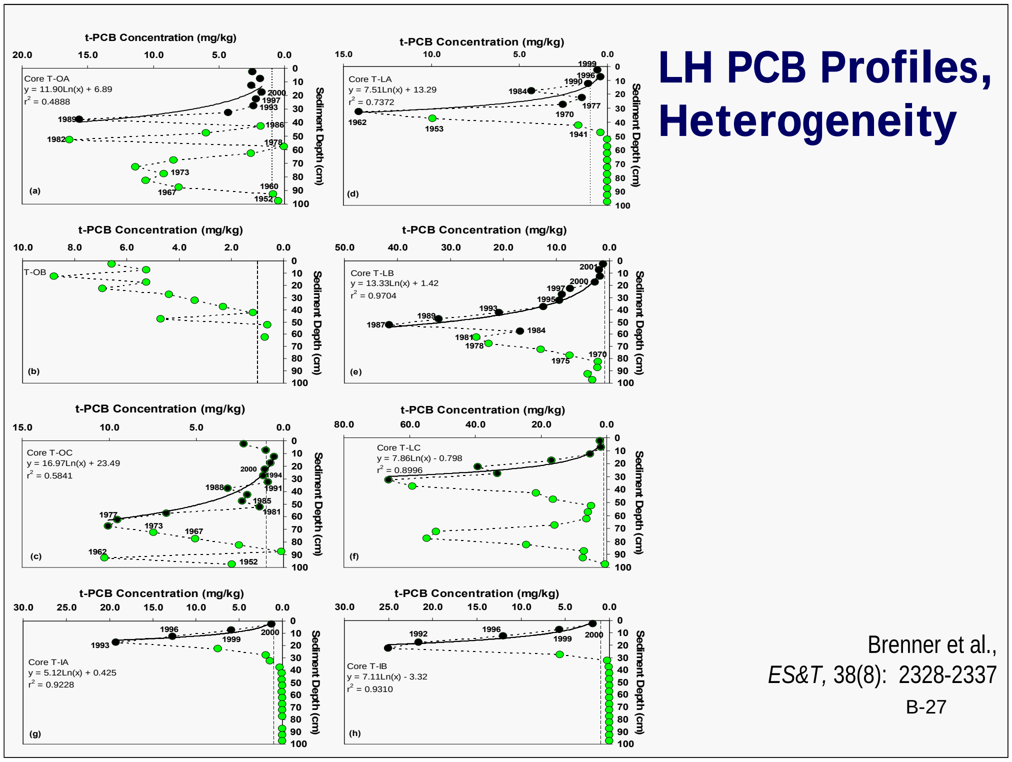
USEPA ORD (Cincinnati, OH) and Region 10

Quantifying Sediment Deposition and Contaminant Burial



B-26

Brenner et al., *ES&T*, 38(8): 2328-2337



LH PCB Profiles, Heterogeneity

Brenner et al.,
ES&T, 38(8): 2328-2337

B-27

Time to Achieve
ROD (U.S. EPA 1994) Cleanup Goals

- ROD surface sediment cleanup goal (1 mg/kg)
- Mean site-specific sediment quality criteria (0.4 mg/kg)
- NOAA effects range-low (0.05 mg/kg)

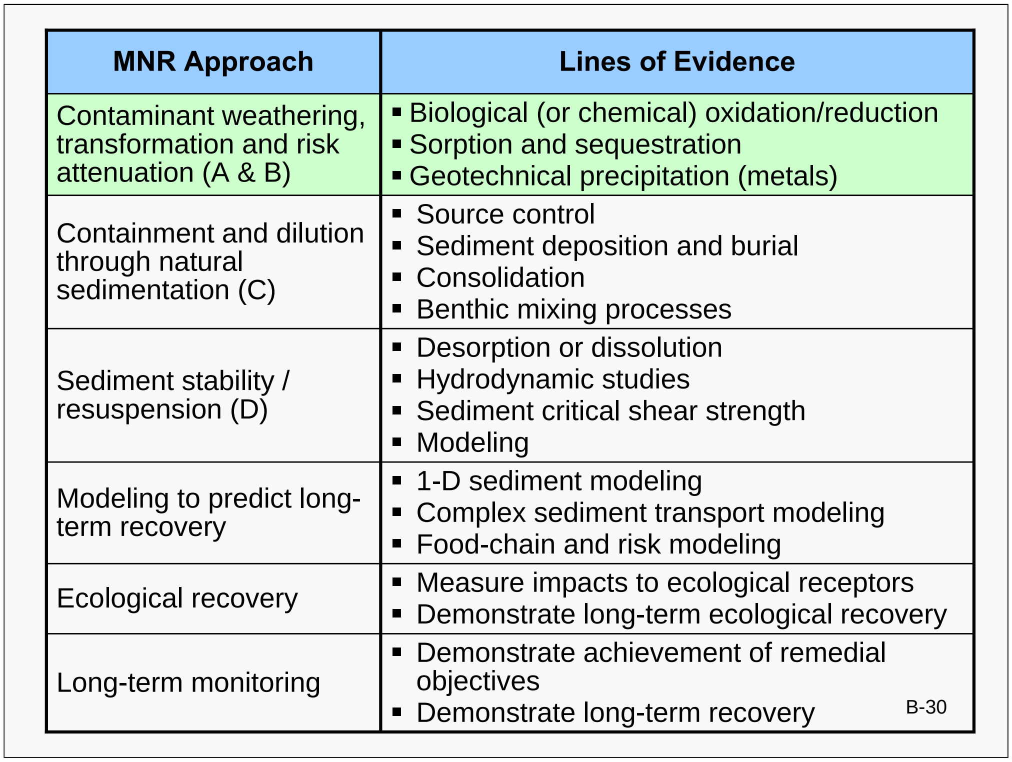
Time to Achieve Cleanup Goals		
1 mg/kg t-PCB	0.4 mg/kg t-PCB	0.05 mg/kg t-PCB
1 – 5 yrs	2 – 10 yrs	10 – 30 yrs

95% confidence levels increased the time frame up to 95 yrs

Brenner et al., *ES&T*, 38(8): 2328-2337

Natural Sedimentation and Burial Summary

- Source control can lead to reduced surface sediment contaminant concentrations
- Coring provides rapid assessment of historical recovery
- Coring also provides highly relevant information in support of other remedies in addition to MNR
  - History of contaminant release
  - Surface sediment concentrations and trends
  - Depositional rates
  - Indications of sediment stability
  - Physical and chemical information about sediments (PSD, TOC, bulk density, AVS, redox, pH)
  - Depth of contamination
- Can be combined with geochronology
  - Age dating sediment cores
  - Sediment deposition rates
  - Benthic mixing



MNR Approach	Lines of Evidence
Contaminant weathering, transformation and risk attenuation (A & B)	▪ Biological (or chemical) oxidation/reduction ▪ Sorption and sequestration ▪ Geotechnical precipitation (metals)
Containment and dilution through natural sedimentation (C)	▪ Source control ▪ Sediment deposition and burial ▪ Consolidation ▪ Benthic mixing processes
Sediment stability / resuspension (D)	▪ Desorption or dissolution ▪ Hydrodynamic studies ▪ Sediment critical shear strength ▪ Modeling
Modeling to predict long-term recovery	▪ 1-D sediment modeling ▪ Complex sediment transport modeling ▪ Food-chain and risk modeling
Ecological recovery	▪ Measure impacts to ecological receptors ▪ Demonstrate long-term ecological recovery
Long-term monitoring	▪ Demonstrate achievement of remedial objectives ▪ Demonstrate long-term recovery

B-30

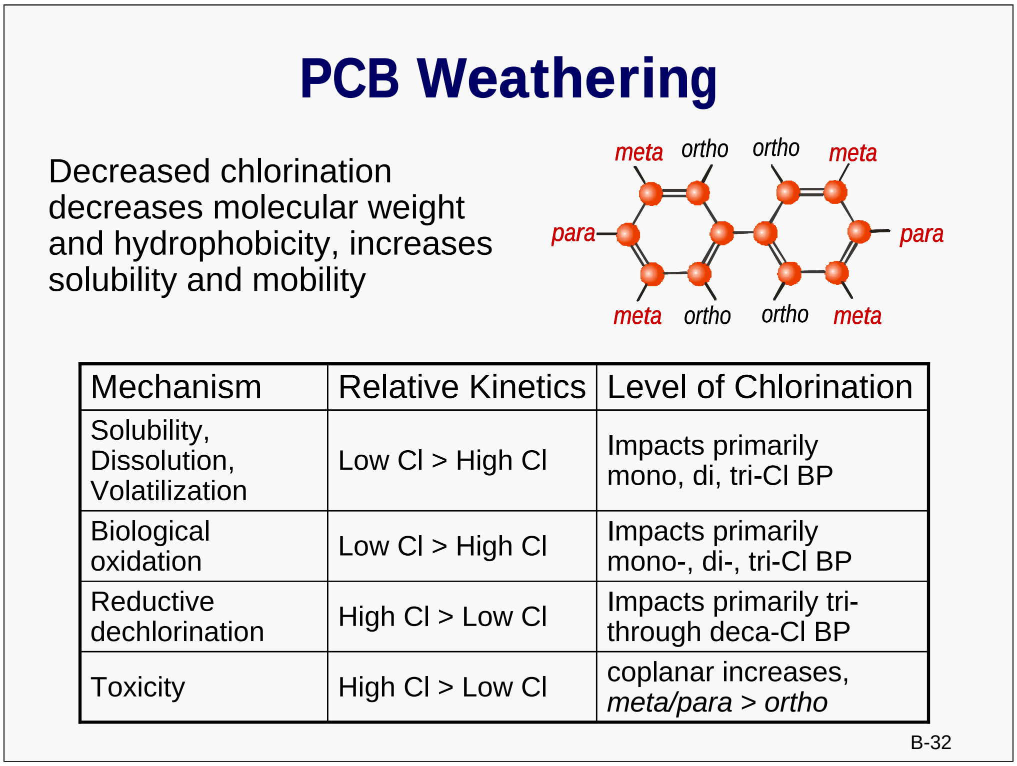
Contaminant Transformation Processes

- Transformation processes (weathering)
  - Sorption/Sequestration
  - Precipitation
  - Dissolution/volatilization
  - Biological transformation
  - Abiotic transformation
- Can lead to chemical detoxification
  - PCB dechlorination
  - PAH degradation
  - Metals precipitation
- Can lead to increased toxicity
  - Mercury methylation
  - Some dioxin dechlorination processes
- Chemical forensics/fingerprinting, multivariate statistics, laboratory studies, in situ studies

Transformation Processes to be Discussed

- PCBs
- PAHs
- Divalent metals and Chromium

B-31



PCB Weathering

Decreased chlorination decreases molecular weight and hydrophobicity, increases solubility and mobility

Mechanism	Relative Kinetics	Level of Chlorination
Solubility, Dissolution, Volatilization	Low Cl > High Cl	Impacts primarily mono, di, tri-Cl BP
Biological oxidation	Low Cl > High Cl	Impacts primarily mono-, di-, tri-Cl BP
Reductive dechlorination	High Cl > Low Cl	Impacts primarily tri- through deca-Cl BP
Toxicity	High Cl > Low Cl	coplanar increases, *meta/para > ortho*

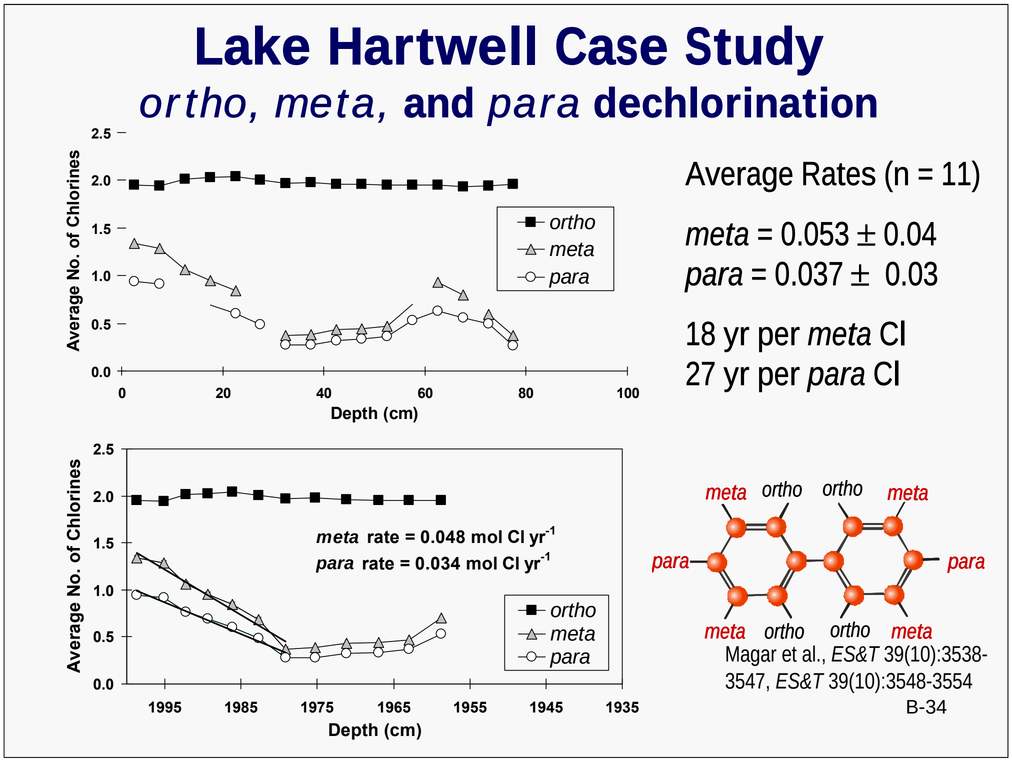
B-32

Lake Hartwell Case Study

Major Congener Shifts Observed in Core L

IUPAC No.	Congener Name	Percent Change
PCB 1	2-chlorobiphenyl	4.4
PCB 4/10	2,2'/2,6-dichlorobiphenyls	29
PCB 8/5	2,4'/2,3-dichlorobiphenyls	5.8
PCB 16/32	2,2',3/2,4',6-trichlorobiphenyls	5.8
PCB 19	2,2',6-trichlorobiphenyl	8.4
PCB 24/27	2,3,6/2,3',6-trichlorobiphenyls	2.5
PCB 66 -156	tetra- through hexachlorobiphenyls	-45

Magar et al., *ES&T* 39(10):3538-3547, *ES&T* 39(10):3548-3554



Lake Hartwell Case Study

ortho, *meta*, and *para* dechlorination

Average Rates (n = 11)

meta = 0.053 ± 0.04
para = 0.037 ± 0.03

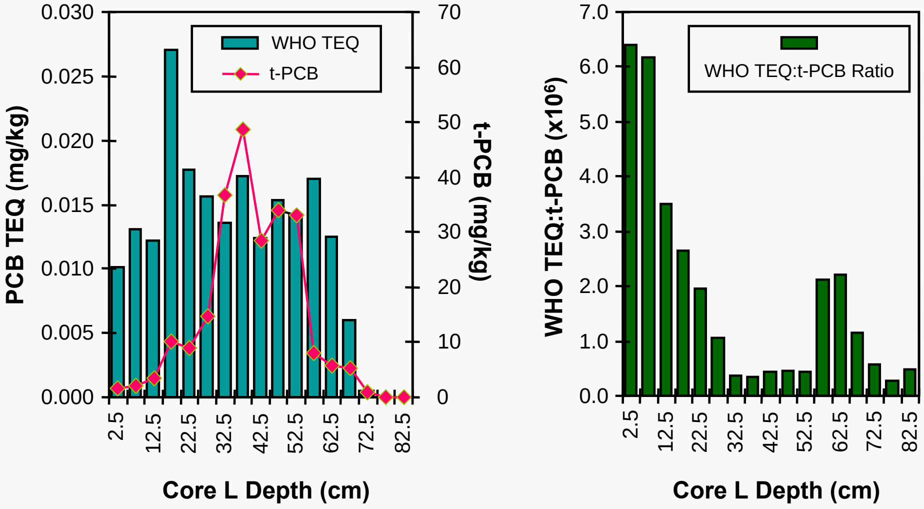
18 yr per *meta* Cl
27 yr per *para* Cl

meta **rate = 0.048 mol Cl yr^{-1}**
para **rate = 0.034 mol Cl yr^{-1}**

Magar et al., *ES&T* 39(10):3538-3547, *ES&T* 39(10):3548-3554

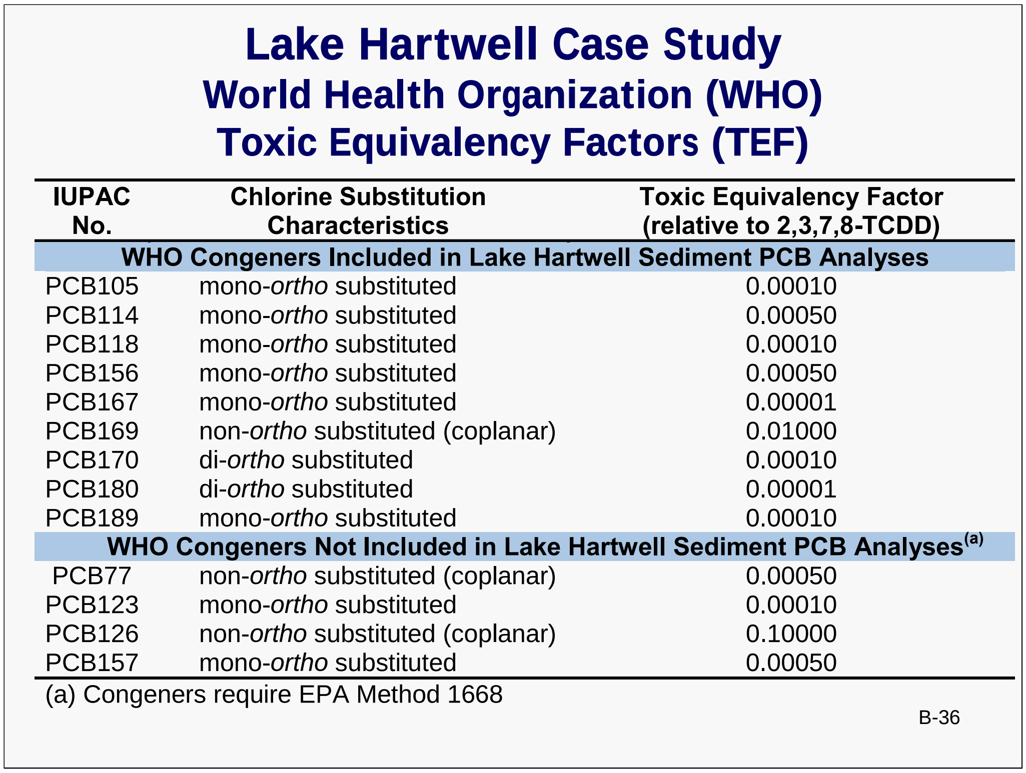
B-34

Lake Hartwell
Toxicity Equivalencies (TEQ)



TEQ values based on World Health Organization (WHO) toxicity equivalency factors (TEF)

B-35



Lake Hartwell Case Study

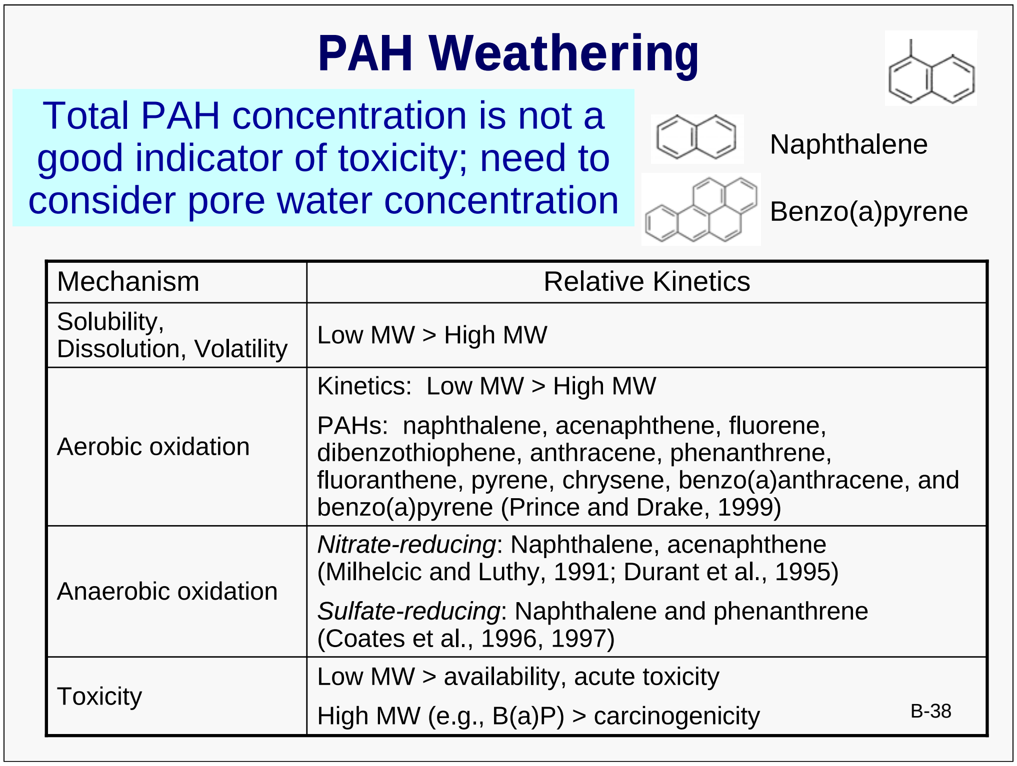
World Health Organization (WHO) Toxic Equivalency Factors (TEF)

IUPAC No.	Chlorine Substitution Characteristics	Toxic Equivalency Factor (relative to 2,3,7,8-TCDD)
WHO Congeners Included in Lake Hartwell Sediment PCB Analyses		
PCB105	mono-*ortho* substituted	0.00010
PCB114	mono-*ortho* substituted	0.00050
PCB118	mono-*ortho* substituted	0.00010
PCB156	mono-*ortho* substituted	0.00050
PCB167	mono-*ortho* substituted	0.00001
PCB169	non-*ortho* substituted (coplanar)	0.01000
PCB170	di-*ortho* substituted	0.00010
PCB180	di-*ortho* substituted	0.00001
PCB189	mono-*ortho* substituted	0.00010
WHO Congeners Not Included in Lake Hartwell Sediment PCB Analyses(a)		
PCB77	non-*ortho* substituted (coplanar)	0.00050
PCB123	mono-*ortho* substituted	0.00010
PCB126	non-*ortho* substituted (coplanar)	0.10000
PCB157	mono-*ortho* substituted	0.00050

(a) Congeners require EPA Method 1668

PCB Weathering and Dechlorination Summary

- Dechlorination processes
  - Tetra–deca PCBs transform to mono–tri PCBs
  - *Ortho*-chlorines (least toxic) are conserved
  - Provides long-term reduced toxicity (short-term relies on burial)
- Toxicity reduction
  - Dechlorination reduces toxicity (fewer chlorines and reduced coplanar congeners)
  - Dechlorination is a progressive process
  - Increasing dechlorination with depth and age
- Natural weathering processes
  - Reduce t-PCB concentrations
  - Primarily impacts lower MW PCBs
  - PCBs may resemble higher MW Aroclors with time



PAH Weathering

Total PAH concentration is not a good indicator of toxicity; need to consider pore water concentration

Naphthalene

Benzo(a)pyrene

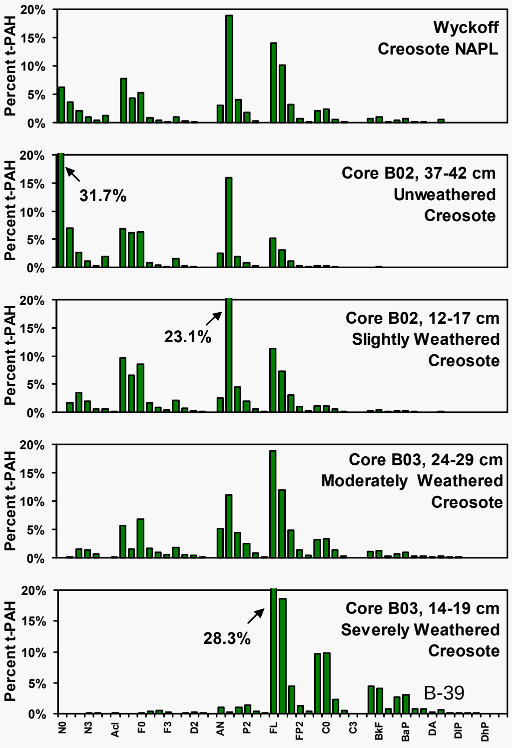
Mechanism	Relative Kinetics
Solubility, Dissolution, Volatility	Low MW > High MW
Aerobic oxidation	Kinetics: Low MW > High MW PAHs: naphthalene, acenaphthene, fluorene, dibenzothiophene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, and benzo(a)pyrene (Prince and Drake, 1999)
Anaerobic oxidation	*Nitrate-reducing*: Naphthalene, acenaphthene (Milhelcic and Luthy, 1991; Durant et al., 1995) *Sulfate-reducing*: Naphthalene and phenanthrene (Coates et al., 1996, 1997)
Toxicity	Low MW > availability, acute toxicity High MW (e.g., B(a)P) > carcinogenicity

PAH Weathering in Creosote-Dominated Samples at Eagle Harbor

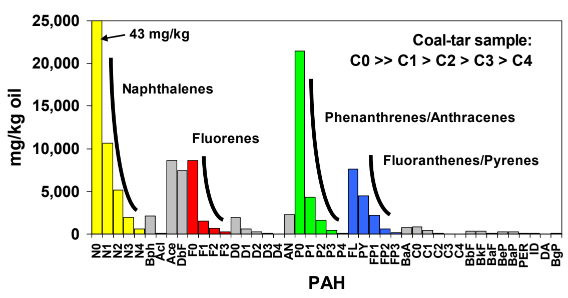
- Rapid loss of Naphthalene and alkyl-naphthalenes
- Progressive loss of 3-ring PAHs and alkyl-derivatives
  - Naphthalene
  - Acenaphthylene
  - Acenaphthene
  - Dibenzofuran
  - Fluorene
  - Anthracene
  - Phenanthrene
  - Dibenzothiophene
- High molecular-weight PAHs are more persistent

Brenner et al., *ES&T*, 36(12): 2605-2613

Stout et al., *J. Env. Forensics, 2*(4): 287-300

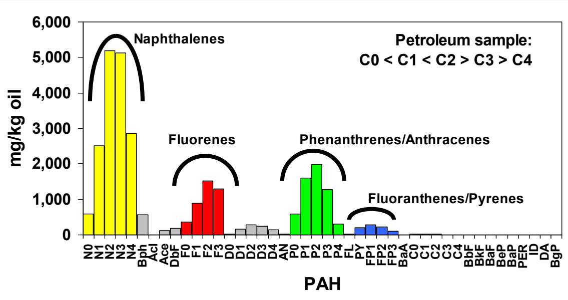


PAH Fingerprinting (Petrogenic vs. Pyrogenic)



Pyrogenic
(e.g., tars and coal byproducts)

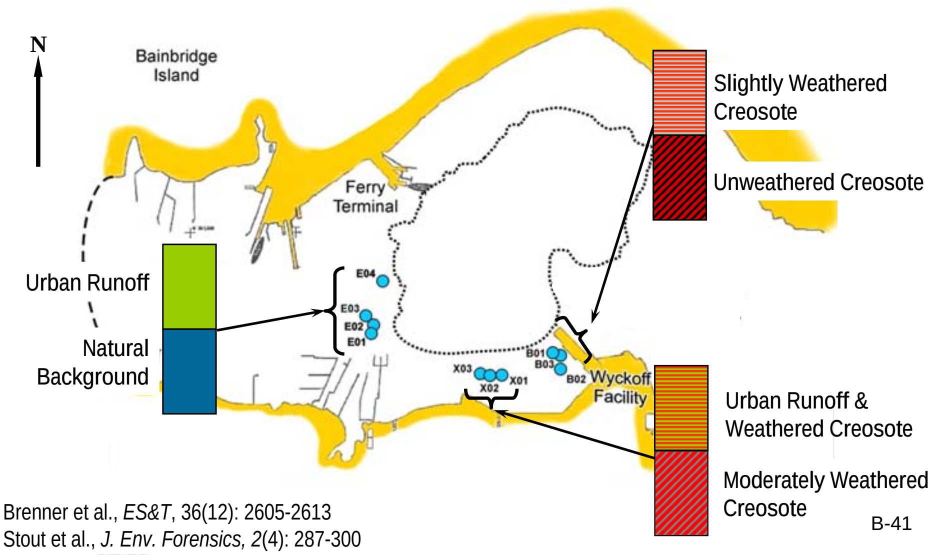
C0 > C1 > C2 > C3 > C4



Petrogenic
(e.g., petroleum products)

C0 < C1 < **C2** > C3 > C4

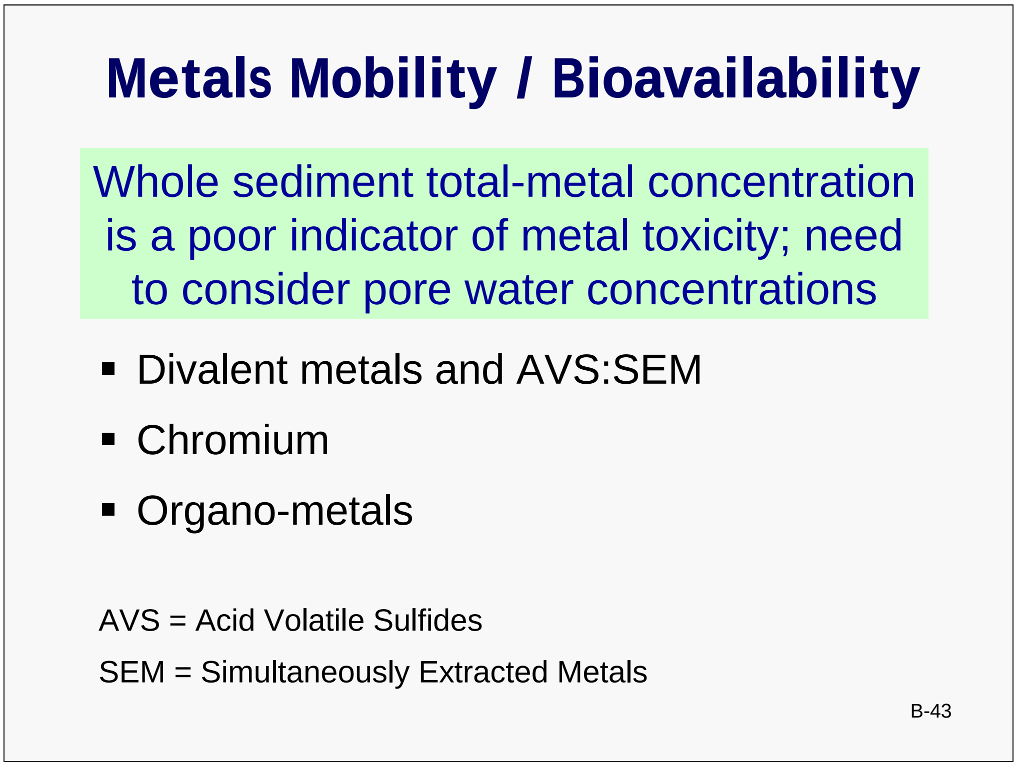
PAH and TPH Characteristics in Eagle Harbor (WA) Sediments



Brenner et al., *ES&T*, 36(12): 2605-2613
Stout et al., *J. Env. Forensics*, *2*(4): 287-300

PAH Weathering Summary

- Degradation
  - Degradation is an oxidative process
  - Evidence for anaerobic oxidation exists
  - Kinetics: Lower-MW PAHs > Higher-MW PAHs
  - ≥4-ring PAHs degrade very slowly (if at all)
- Toxicity reduction
  - Degradation reduces highly mobile low MW PAHs
  - Reduces acute PAH toxicity due to 2- and 3-ring PAHs
  - PAH in pore water is a much better indicator of toxicity than whole sediment PAH concentration
- Natural weathering processes
  - Primarily impacts lower MW PAHs
  - Virtually indistinguishable from degradation
  - Can make source identification difficult



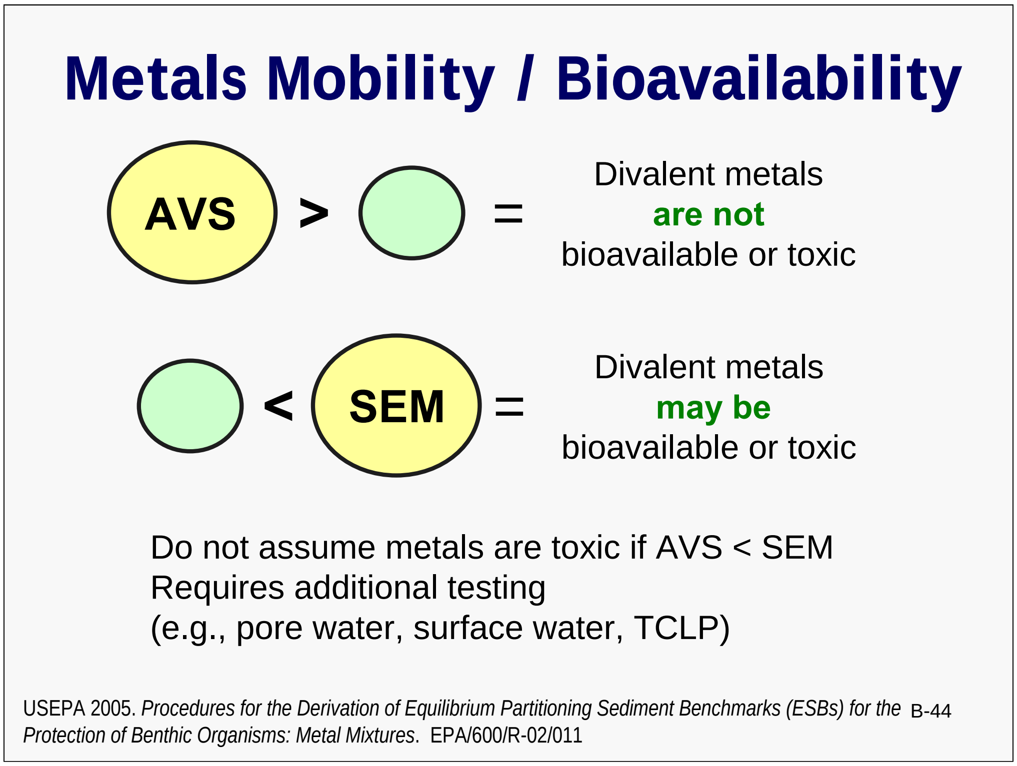
Metals Mobility / Bioavailability

Whole sediment total-metal concentration is a poor indicator of metal toxicity; need to consider pore water concentrations

- Divalent metals and AVS:SEM
- Chromium
- Organo-metals

AVS = Acid Volatile Sulfides

SEM = Simultaneously Extracted Metals



Metals Mobility / Bioavailability

AVS > ● =

Divalent metals
are not
bioavailable or toxic

● < **SEM** =

Divalent metals
may be
bioavailable or toxic

Do not assume metals are toxic if AVS < SEM
Requires additional testing
(e.g., pore water, surface water, TCLP)

USEPA 2005. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures*. EPA/600/R-02/011

Metals Mobility / Bioavailability

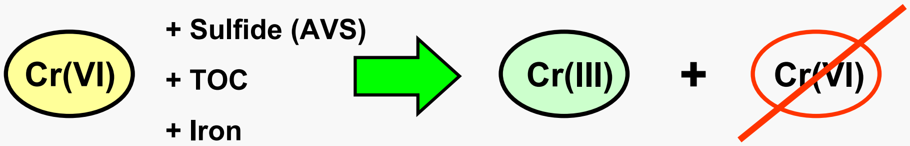
- If SEM > AVS, check pore water concentrations

$$\frac{\sum \mathrm{M}_{i,d}}{\mathrm{FCV}_{i,d}} \leq 1 \quad \Rightarrow \quad non-toxic$$

  - M = Metal interstitial (pore water) molar concentration (Cadmium, Copper, Lead, Nickel, Silver and Zinc)
  - FCV = Final chronic value
  - SCV = Secondary chronic value if FCV is unavailable

USEPA 2005. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures*. EPA/600/R-02/011

Chromium Bioavailability and Toxicity in Sediments



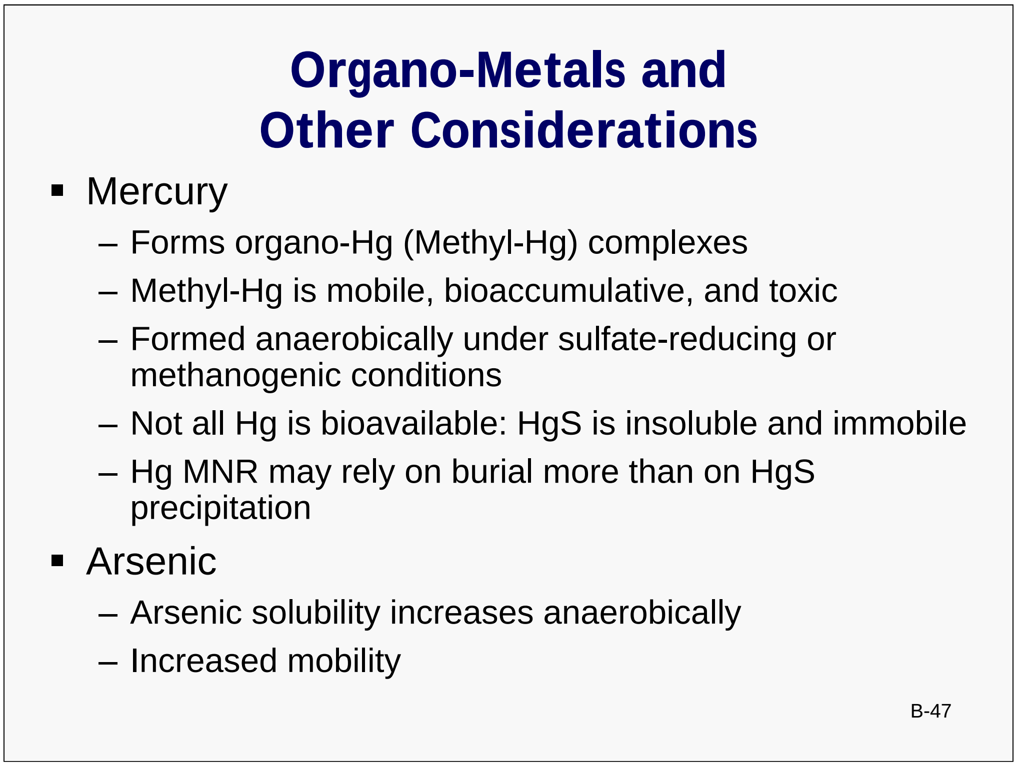
Cr(VI)

+ Sulfide (AVS)
+ TOC
+ Iron

Cr(III) + ~~Cr(VI)~~

- Cr(VI) is soluble and exhibits greater toxicity than Cr(III)
- Cr(VI) is transformed to Cr(III) under reducing conditions
- Cr(III) is relatively insoluble & thermodynamically stable
- Cr(III) is the dominant chromium species in sediment
- Cr(III) exhibits very low mobility and toxicity

USEPA, 2005; Berry et al., 2004; Hansel et al., 2004
Walter Berry is with USEPA Narragansett Bay labs

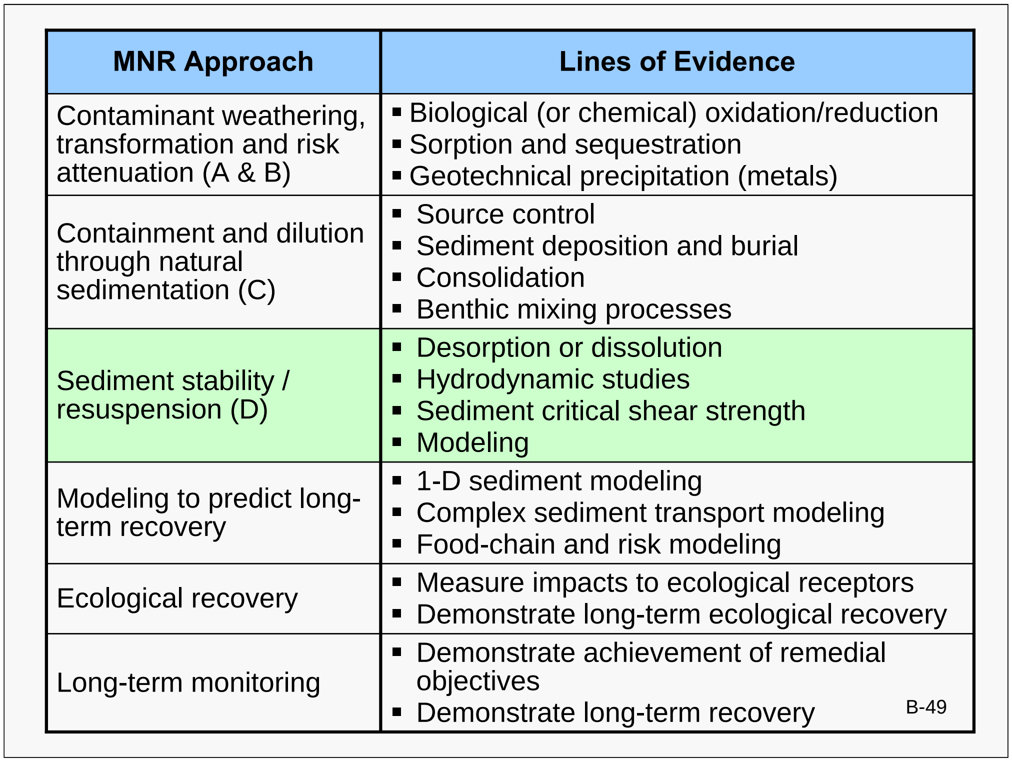


Organo-Metals and Other Considerations

- Mercury
  - Forms organo-Hg (Methyl-Hg) complexes
  - Methyl-Hg is mobile, bioaccumulative, and toxic
  - Formed anaerobically under sulfate-reducing or methanogenic conditions
  - Not all Hg is bioavailable: HgS is insoluble and immobile
  - Hg MNR may rely on burial more than on HgS precipitation
- Arsenic
  - Arsenic solubility increases anaerobically
  - Increased mobility

Metals Summary

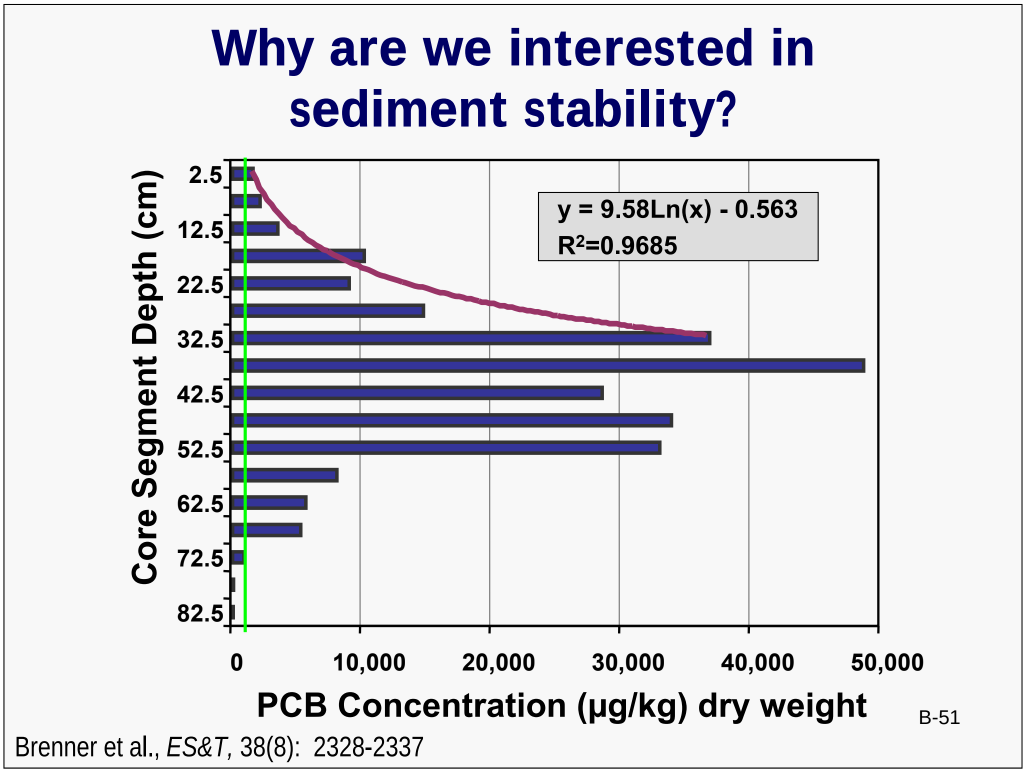
- MNR for divalent metals relies primarily on reduction and precipitation to non-toxic Me-S precipitates
- MNR for chromium relies on anaerobic reduction to immobile and non-toxic Cr(III)
- AVS/SEM is used to screen toxicity
- **Pore water** measurements are used to measure bioavailability directly
- Burial also contributes to MNR, particularly for Hg and possibly Se



MNR Approach	Lines of Evidence
Contaminant weathering, transformation and risk attenuation (A & B)	▪ Biological (or chemical) oxidation/reduction ▪ Sorption and sequestration ▪ Geotechnical precipitation (metals)
Containment and dilution through natural sedimentation (C)	▪ Source control ▪ Sediment deposition and burial ▪ Consolidation ▪ Benthic mixing processes
Sediment stability / resuspension (D)	▪ Desorption or dissolution ▪ Hydrodynamic studies ▪ Sediment critical shear strength ▪ Modeling
Modeling to predict long-term recovery	▪ 1-D sediment modeling ▪ Complex sediment transport modeling ▪ Food-chain and risk modeling
Ecological recovery	▪ Measure impacts to ecological receptors ▪ Demonstrate long-term ecological recovery
Long-term monitoring	▪ Demonstrate achievement of remedial objectives ▪ Demonstrate long-term recovery

Sediment Stability

- USEPA 2005 *Guidance*
  - Sediment need not be “stable” per se
  - Focus should be on potential for the creation of unacceptable future risk of exposure to contaminants if/when sediment moves
  - Sediments can move without causing unacceptable increases in risk
- Measuring sediment stability: A balance of forces
  - Sediment critical shear strength
  - Hydrodynamic shear stress



Why are we interested in sediment stability?

B-51

Brenner et al., *ES&T*, 38(8): 2328-2337

Sediment Stability

- Tier 1: Estimate sediment erosion potential based on conventional sediment and hydrodynamic properties
  - Bulk density
  - Sediment grain size
  - Surface water velocities based on available hydrodynamic data
  - Rainfall records and USGS records
- Tier 2: Calculate sediment erosion potential using direct sediment shear strength and current velocity measurements
  - Critical shear strength
  - Bulk density
  - Current and wave velocity measurements
  - Long-term hydrodynamic measurements (e.g. tide gauges)
  - Modeled high-energy events (e.g., 100-year storms)

Mass balance approach

Net depositional: *Mass In > Mass Out*

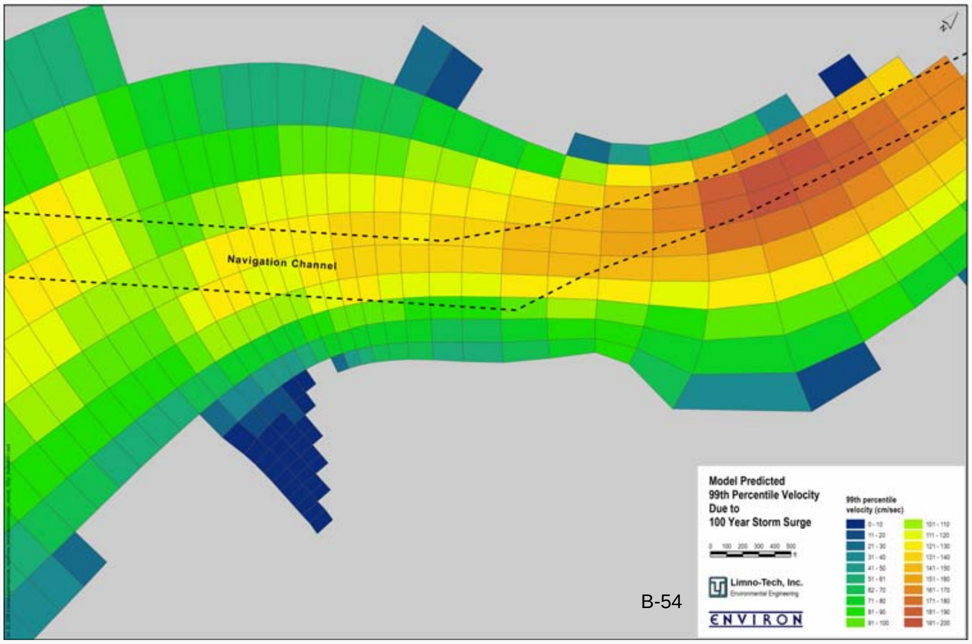
Net erosional: *Mass In < Mass Out*

B-52

Measuring Sediment Stability

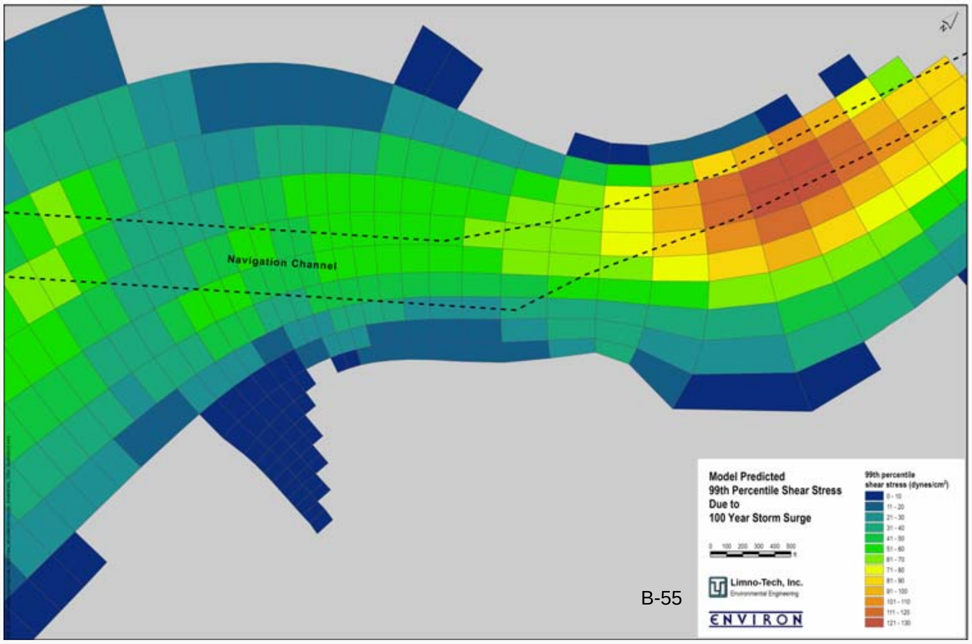
- Sediment shear strength
  - Cohesive, consolidated sediments require direct measurement of critical shear strength
  - Measure in situ current velocities
  - Predict long-term hydrodynamic velocities and corresponding shear forces
    - Normal currents
    - High-energy events (e.g., 100-year storms)
    - Waves (natural, storm, or wind-induced)
    - Navigation (prop wash)
- Sedimentary processes
  - Surface water hydrodynamic shear forces
  - Sediment scour potential (resisted by sediment mass, cohesive forces, and consolidation)
  - Bedload transport
  - Surface sediment coarsening

Peak (100-Year) Storm Surge Velocities



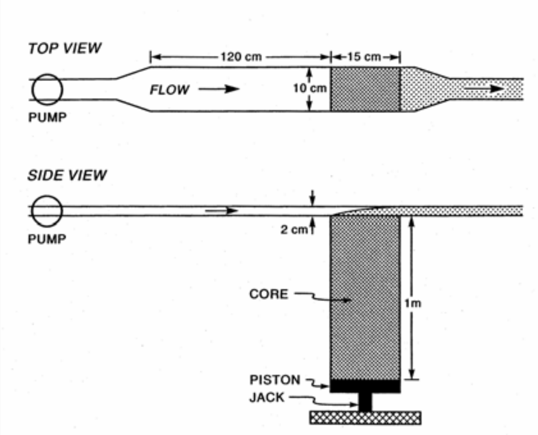
B-54

Peak (100-Year) Storm Hydrodynamic Shear



B-55

Measure Sediment Shear Strength

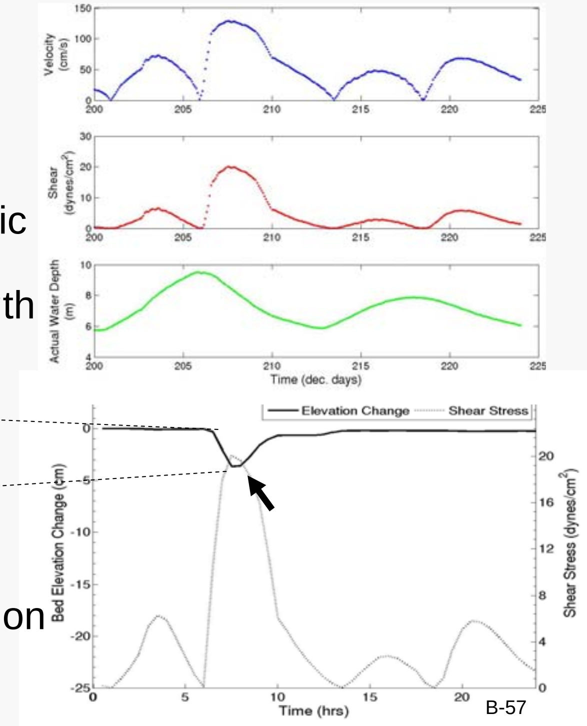


SedFlume

Courtesy of Sea Engineering, Inc. (Santa Cruz, CA)

Predicting Sediment Scour Potential

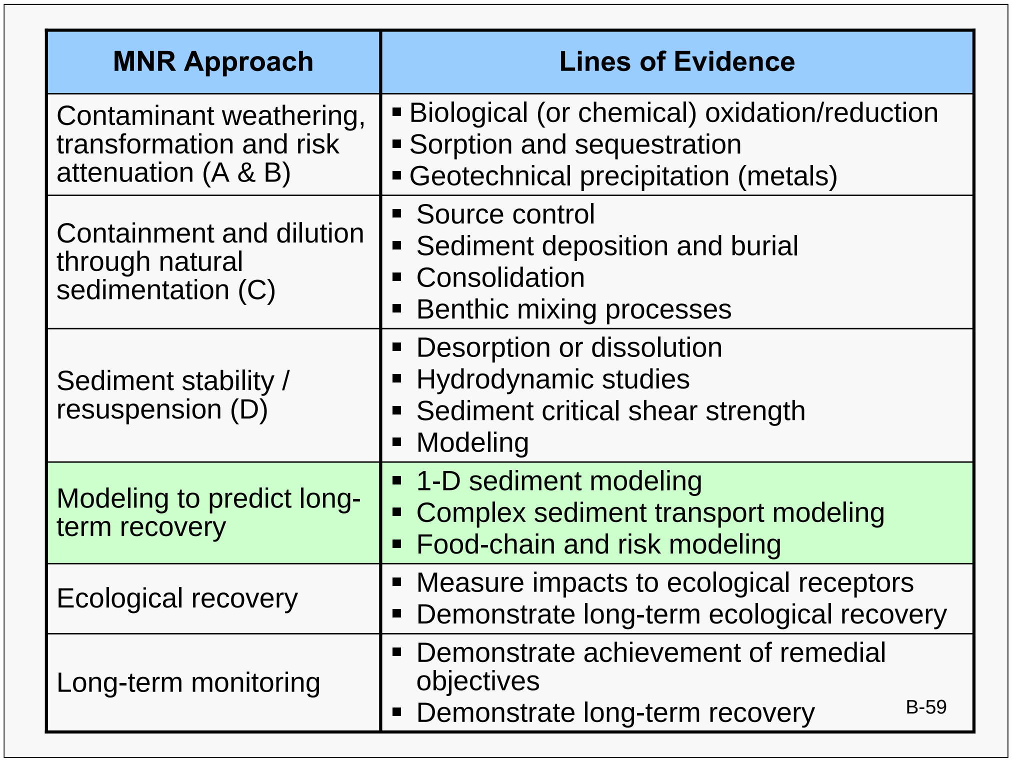
- Combine hydrodynamic shear stress and sediment shear strength measurements
- 100-year storm scour potential: ~3 cm
- Rebound due to sediment deposition
- Site specific and location specific



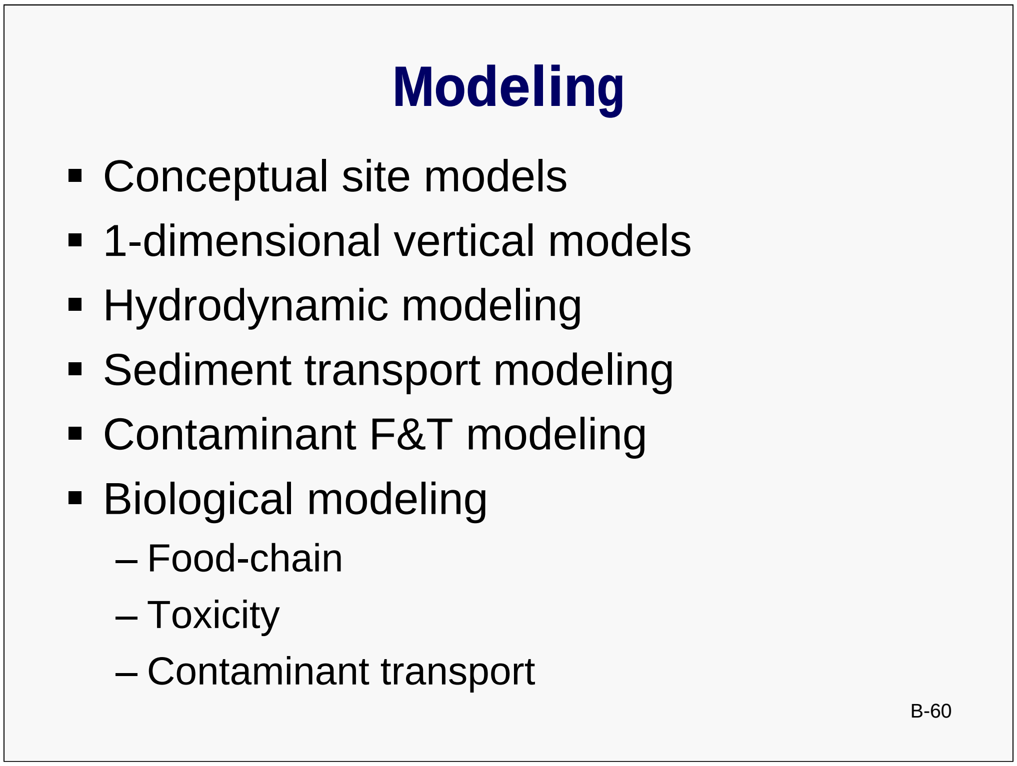
B-57

Sediment Scour Potential Summary

- What is the potential for sediment scour?
- Does sediment scour risk exposure of higher (unacceptable) surface sediment concentrations?
- What are appropriate responses to sediment scour?
  - Long-term monitoring and risk assessment
  - Preventive measures such as capping or armoring
  - When is dredging an appropriate preventative measure?



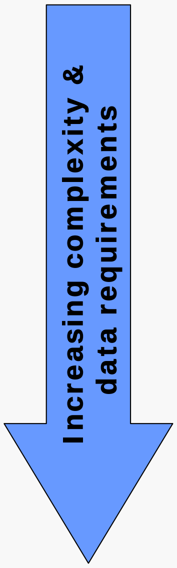
MNR Approach	Lines of Evidence
Contaminant weathering, transformation and risk attenuation (A & B)	▪ Biological (or chemical) oxidation/reduction ▪ Sorption and sequestration ▪ Geotechnical precipitation (metals)
Containment and dilution through natural sedimentation (C)	▪ Source control ▪ Sediment deposition and burial ▪ Consolidation ▪ Benthic mixing processes
Sediment stability / resuspension (D)	▪ Desorption or dissolution ▪ Hydrodynamic studies ▪ Sediment critical shear strength ▪ Modeling
Modeling to predict long-term recovery	▪ 1-D sediment modeling ▪ Complex sediment transport modeling ▪ Food-chain and risk modeling
Ecological recovery	▪ Measure impacts to ecological receptors ▪ Demonstrate long-term ecological recovery
Long-term monitoring	▪ Demonstrate achievement of remedial objectives ▪ Demonstrate long-term recovery



Modeling

- Conceptual site models
- 1-dimensional vertical models
- Hydrodynamic modeling
- Sediment transport modeling
- Contaminant F&T modeling
- Biological modeling
  - Food-chain
  - Toxicity
  - Contaminant transport

Fate & Transport Modeling



1. Hydrodynamic – simple statistical model

   Provides basic information about flow direction and factors governing hydraulics at the site

2. Hydrodynamic – detailed numerical model

   Predicts flow direction and magnitude under site-specific conditions, establishing links between sources and deposition

3. Hydrodynamic with particle transport

   Predicts sediment particle transport pathways

4. Mechanistic Sediment Transport

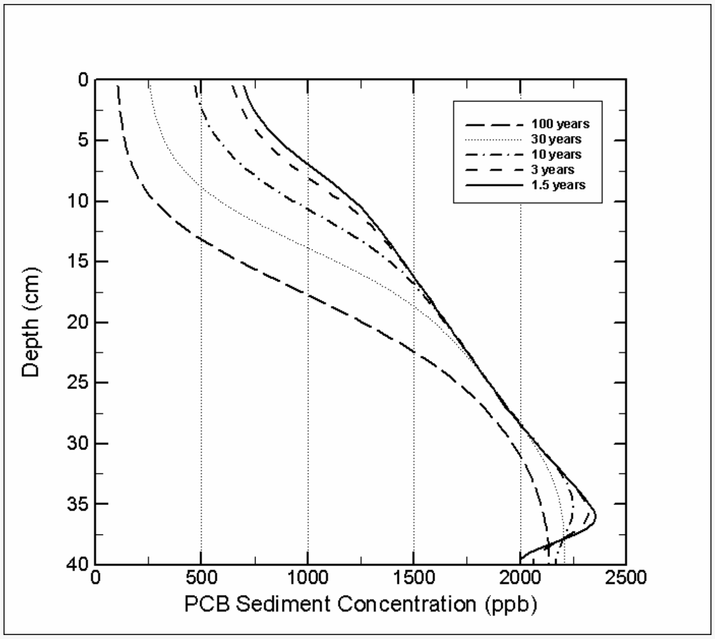
   Provides quantitative estimates of the magnitude and direction of sediment transport, short-term and long-term, calibrated to water column solid loads and geochronological data

5. Contaminant Fate and Transport

   Provides quantitative estimates of amount and direction of dissolved and sediment-bound contaminant transport, short-term and long-term, calibrated to water column loads, sediment bed concentrations, etc.

Courtesy of Tim Dekker (LimnoTech, Inc., Ann Arbor, MI)

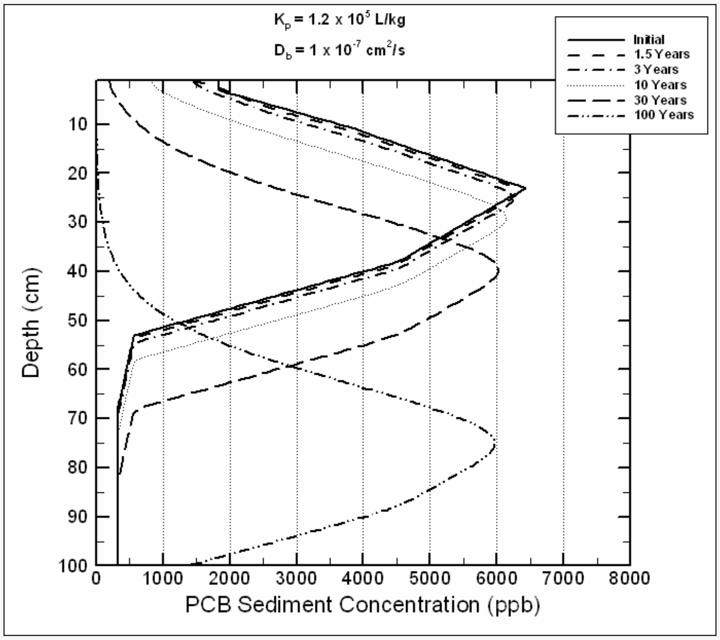
Modeling Long-Term Sediment Recovery (Case 1: No Deposition)



B-62

Courtesy of Craig Jones (Sea Engineering, Inc., Santa Cruz, CA)

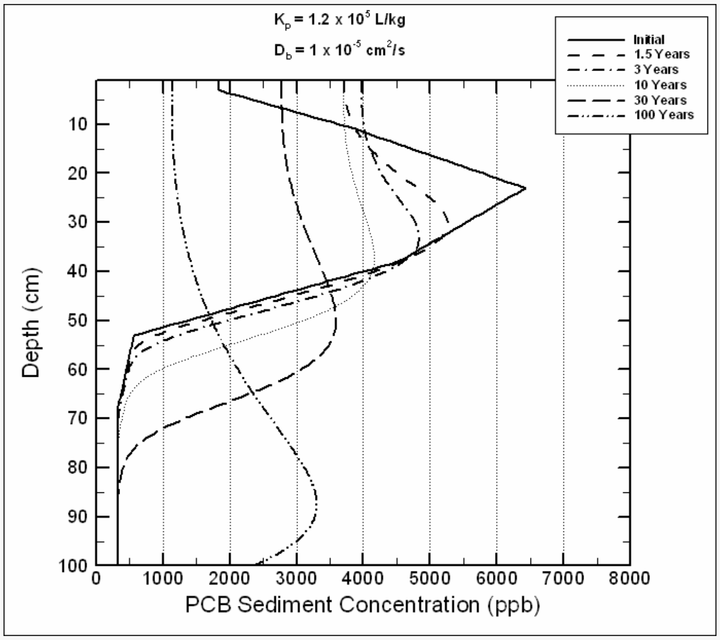
Modeling Long-Term Sediment Recovery (Case 2: Deposition = 0.5 cm/yr; normal mixing)



B-63

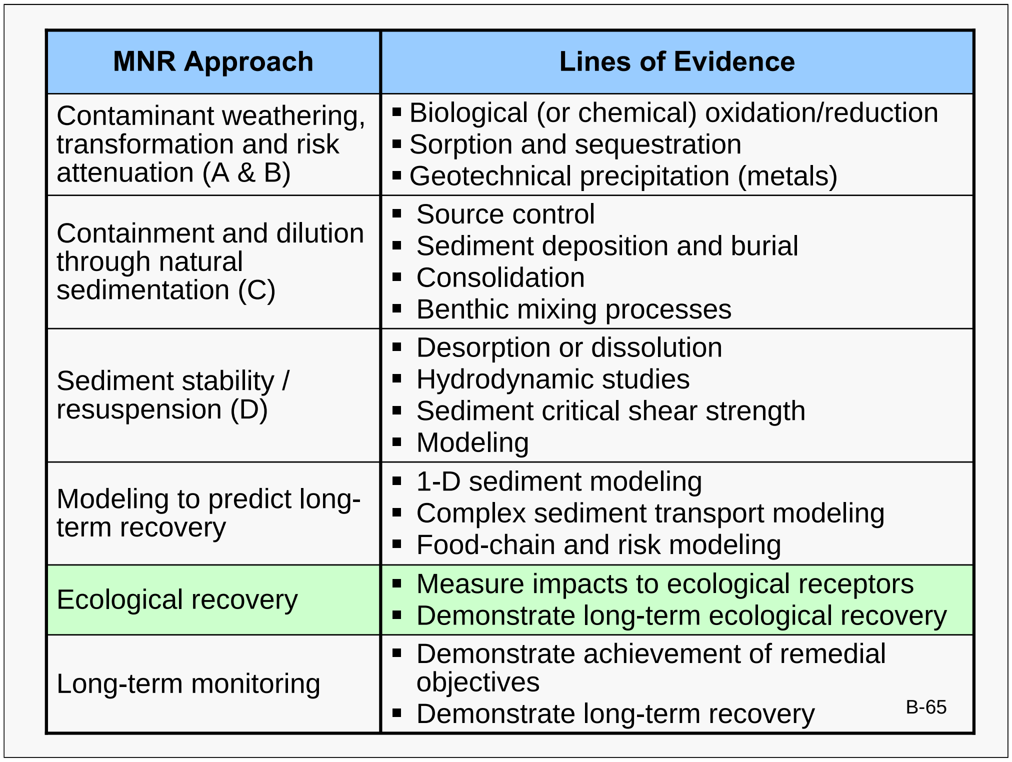
Courtesy of Craig Jones (Sea Engineering, Inc., Santa Cruz, CA)

Modeling Long-Term Sediment Recovery
(Case 3: Deposition = 0.5 cm/yr; heavy mixing)



B-64

Courtesy of Craig Jones (Sea Engineering, Inc., Santa Cruz, CA)



MNR Approach	Lines of Evidence
Contaminant weathering, transformation and risk attenuation (A & B)	▪ Biological (or chemical) oxidation/reduction ▪ Sorption and sequestration ▪ Geotechnical precipitation (metals)
Containment and dilution through natural sedimentation (C)	▪ Source control ▪ Sediment deposition and burial ▪ Consolidation ▪ Benthic mixing processes
Sediment stability / resuspension (D)	▪ Desorption or dissolution ▪ Hydrodynamic studies ▪ Sediment critical shear strength ▪ Modeling
Modeling to predict long-term recovery	▪ 1-D sediment modeling ▪ Complex sediment transport modeling ▪ Food-chain and risk modeling
Ecological recovery	▪ Measure impacts to ecological receptors ▪ Demonstrate long-term ecological recovery
Long-term monitoring	▪ Demonstrate achievement of remedial objectives ▪ Demonstrate long-term recovery

Measuring Ecological Recovery

- Ecological recovery is likely to lag behind sediment recovery
- Establish meaningful and achievable goals
- Monitor above statistical variability

Balancing Multiple Lines of Evidence

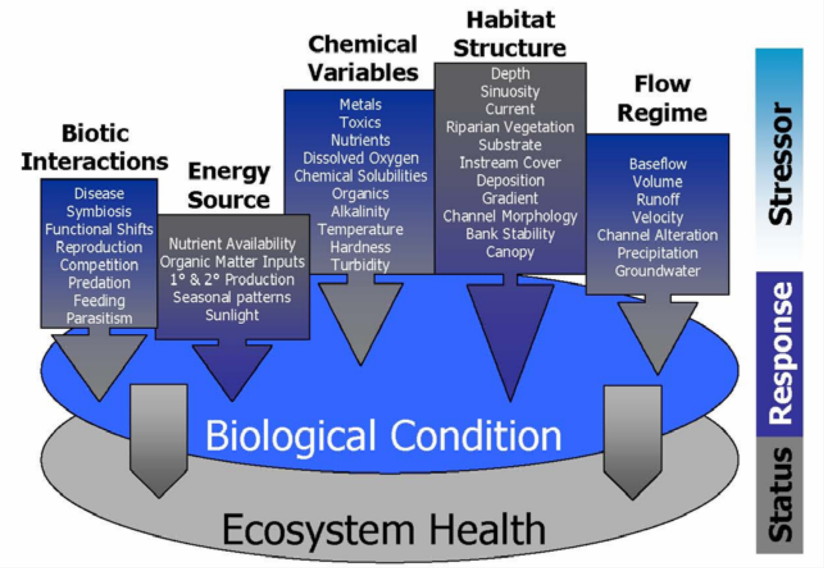
Monitoring Ecological Recovery

- Establish meaningful, achievable goals
- Ecological recovery is likely to lag behind sediment recovery
- Monitor above statistical variability

Balancing Multiple Lines of Evidence

- Source identification
- Nature vs. anthropogenic
- Distinguishing chemical vs. non-chemical stressors
- Detecting ecological changes with time
- Causality
- Risk assessment and ecological exposure

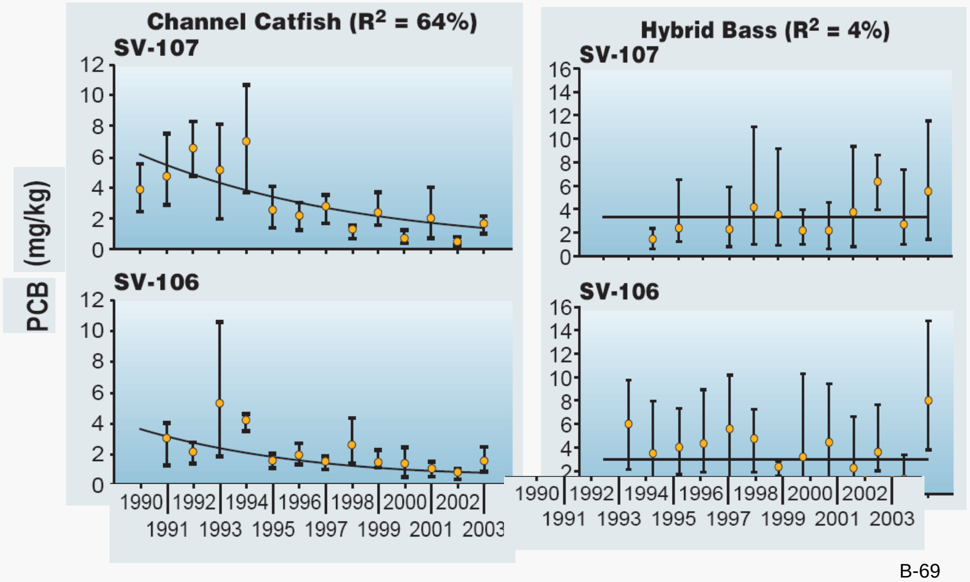
Assessing Ecological Health



Source: TetraTech (2005) Biological Assessment of the Patapsco River Tributary Watersheds
http://www.co.ho.md.us/DPW/DOCS/patapsco.pdf#search=%22fish%20trends%20in%20Patapsco%20River%22

B-68

Lake Hartwell Long-Term Monitoring



Channel Catfish (R^2 = 64%)

Hybrid Bass (R^2 = 4%)

B-69

Booth, P. et al., SETAC 2004, Portland, OR

Training Outline

1. The role of natural recovery in the environment
2. MNR definitions
3. EPA 2005 *Sediment Guidance* Summary
4. Identify and describe MNR lines of evidence
5. Integrating MNR into remedy decision making

Recipe for Successful Environmental Assessment

- Rigorous source characterization to understand source control and long-term contamination potential
- Characterize surface sediment deposition processes
  - Long-term concentration changes
  - Role of surface sediment in ecological exposure and risk
  - Containment of buried contaminants
- Understand hydrodynamics
- Characterize contaminant transformation processes
- Understand bioaccumulation (biota), biological and human health effects, and risk
- Quantify sediment scour potential
- Characterize chemical / geochemical stability

Remedy Comparisons

- Compare MNR with capping and dredging
  - What is a “reasonable time frame” for MNR?
  - Compare to the realistic time tables for dredging and/or capping to be fully implemented
  - When are risk-levels acceptable for MNR?
  - Balancing costs: Is it worth accelerating MNR?
- When Should I Consider/Use MNR?
  - Natural processes are **always** ongoing
  - Maximize MNR to **reduce negative impacts** of more aggressive remedies
  - Make sure remedies **complement** MNR processes
  - **Integrate** MNR with other remedies
  - Monitor to **reduce uncertainty**

What About Enhanced MNR?

- Sediment capping
  - Isolates sediment contaminants
  - Creates a relatively clean sediment surface
- Thin layer capping can accelerate surface sediment concentration reductions, and achievement of cleanup goals
- Novel materials (e.g., carbon) may reduce bioavailability

B-74

EPA/OSRTI Sediment Remedies: Monitored Natural Recovery at
Contaminated Sediment Sites

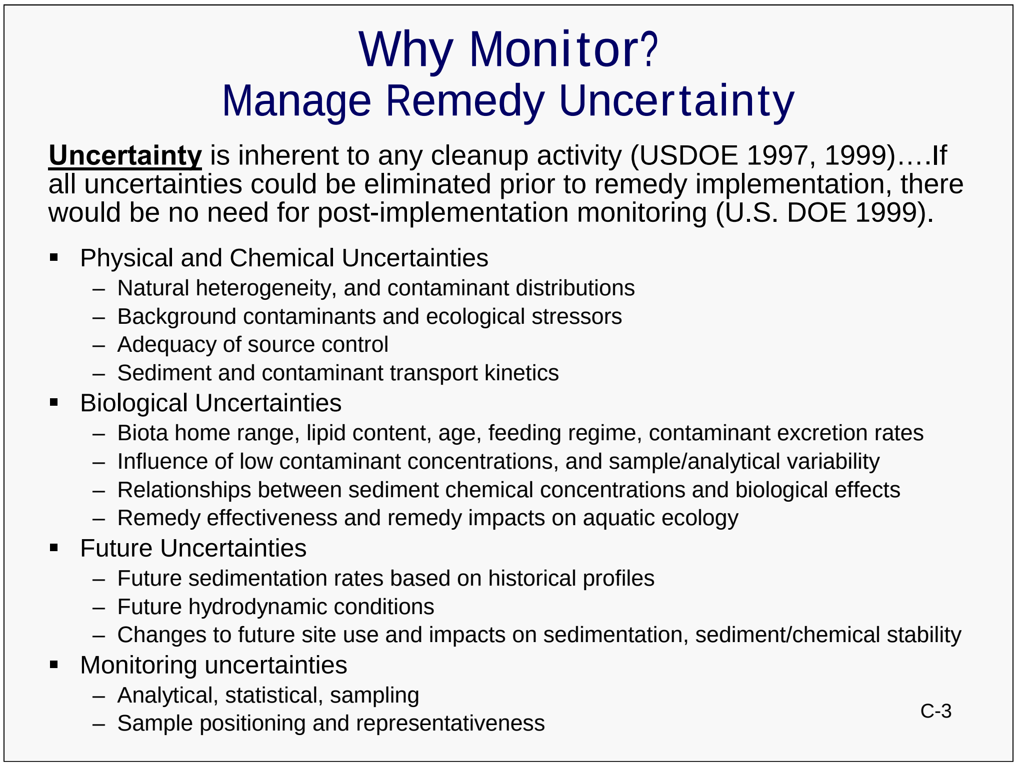
Monitoring Sediment Remedies and Ecological Recovery

Leah H. Evison, PhD
USEPA – Office of Superfund Remediation & Technology Innovation
Evison.leah@epa.gov
(312) 886-7193

Victor S. Magar, PhD, PE
ENVIRON – Chicago, IL
vmagar@environcorp.com
(312) 853-9430

Training Objectives

1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
    - MNR
    - Capping
    - Dredging
3. Present EPA's six-step monitoring DQO process
4. Identify monitoring tools
5. Wyckoff/Eagle Harbor case study
6. Summary



Why Monitor?

Manage Remedy Uncertainty

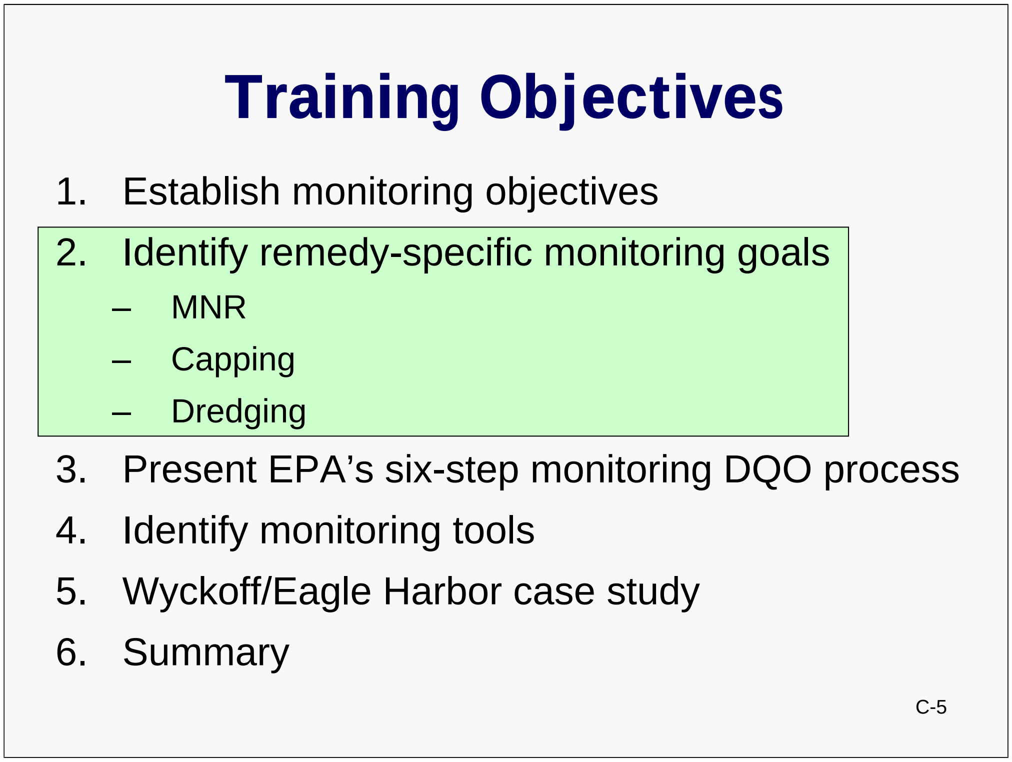
Uncertainty is inherent to any cleanup activity (USDOE 1997, 1999)….If all uncertainties could be eliminated prior to remedy implementation, there would be no need for post-implementation monitoring (U.S. DOE 1999).

- Physical and Chemical Uncertainties
  - Natural heterogeneity, and contaminant distributions
  - Background contaminants and ecological stressors
  - Adequacy of source control
  - Sediment and contaminant transport kinetics
- Biological Uncertainties
  - Biota home range, lipid content, age, feeding regime, contaminant excretion rates
  - Influence of low contaminant concentrations, and sample/analytical variability
  - Relationships between sediment chemical concentrations and biological effects
  - Remedy effectiveness and remedy impacts on aquatic ecology
- Future Uncertainties
  - Future sedimentation rates based on historical profiles
  - Future hydrodynamic conditions
  - Changes to future site use and impacts on sedimentation, sediment/chemical stability
- Monitoring uncertainties
  - Analytical, statistical, sampling
  - Sample positioning and representativeness

Distinguishing Construction, Short-Term and Long-Term Monitoring

- Construction / Performance Monitoring
  - Remedy construction and implementation
  - Acute construction risks to community, ecology, and workers
  - Treatment and operation facilities during implementation
- Short-term
  - Remedy during shake-down period (e.g., one year)
  - Engineering site controls during shake-down period
  - First 5-year review
- Long-term
  - Monitoring and maintenance of institutional controls
  - Long-term monitoring, sampling, testing, analysis, and reporting
  - Long-term maintenance of remedy and engineering site controls

The goal of long-term monitoring is *not* to re-characterize the site at each monitoring event



Training Objectives

1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
    - MNR
    - Capping
    - Dredging
3. Present EPA’s six-step monitoring DQO process
4. Identify monitoring tools
5. Wyckoff/Eagle Harbor case study
6. Summary

Remedy-Specific Monitoring

Primary Remedy Functions

MNR

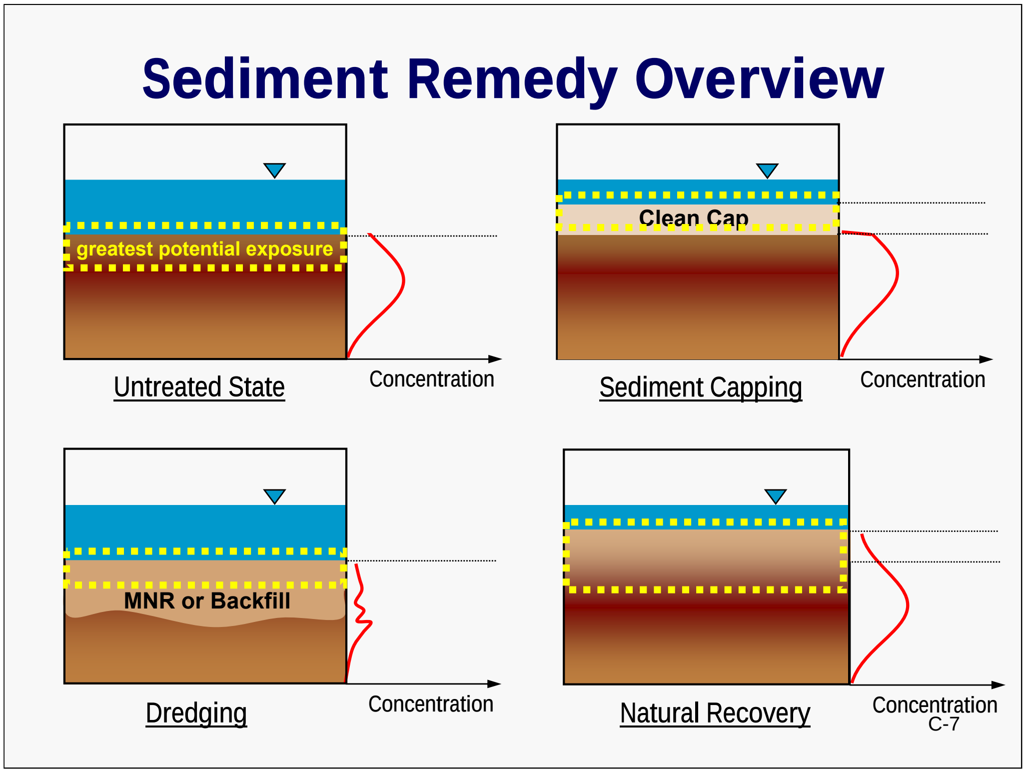
- Chemical transformation
- Chemical sequestration
- Natural sedimentation and burial

Capping

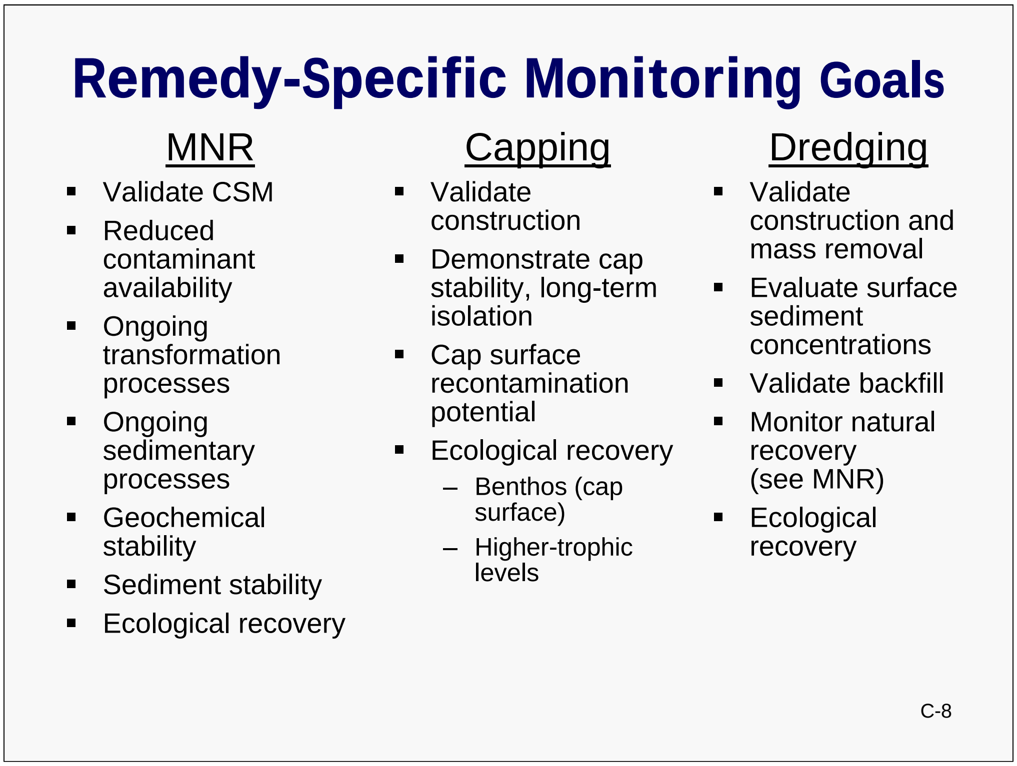
- Burial and isolation
- Chemical sequestration
- Creation of a clean sediment surface

Dredging

- Sediment and contaminant removal
- Reduce contaminant mass in sediment
- Often combine with MNR or backfill to achieve RAOs



Sediment Remedy Overview



Remedy-Specific Monitoring Goals

MNR

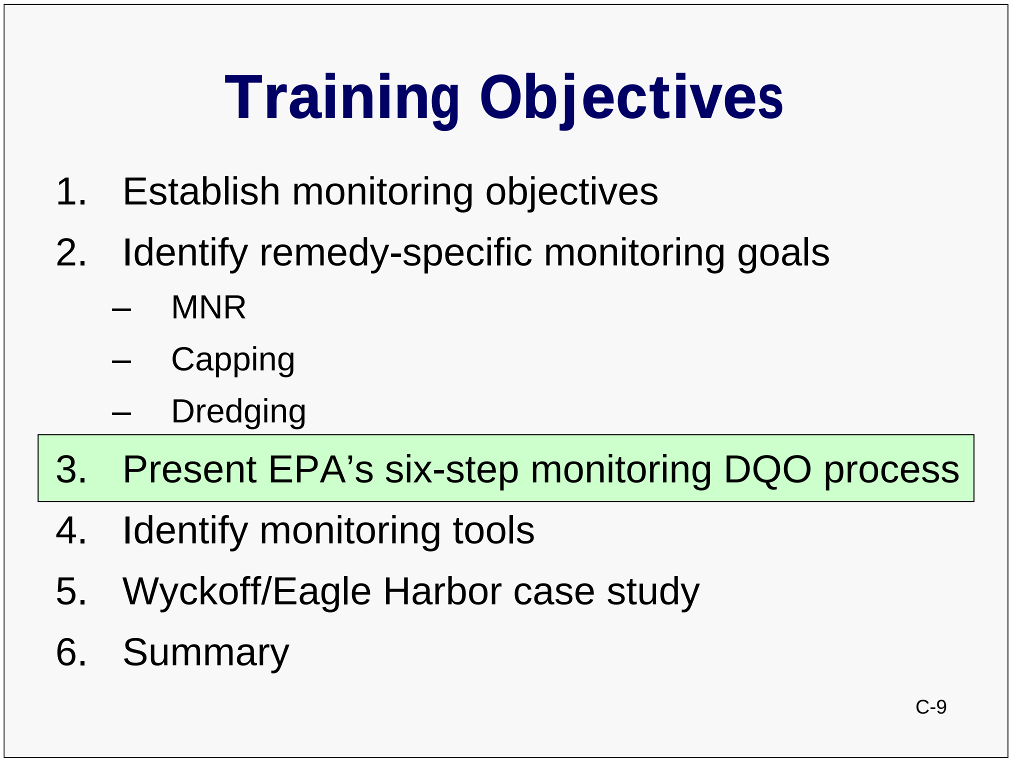
- Validate CSM
- Reduced contaminant availability
- Ongoing transformation processes
- Ongoing sedimentary processes
- Geochemical stability
- Sediment stability
- Ecological recovery

Capping

- Validate construction
- Demonstrate cap stability, long-term isolation
- Cap surface recontamination potential
- Ecological recovery
  - Benthos (cap surface)
  - Higher-trophic levels

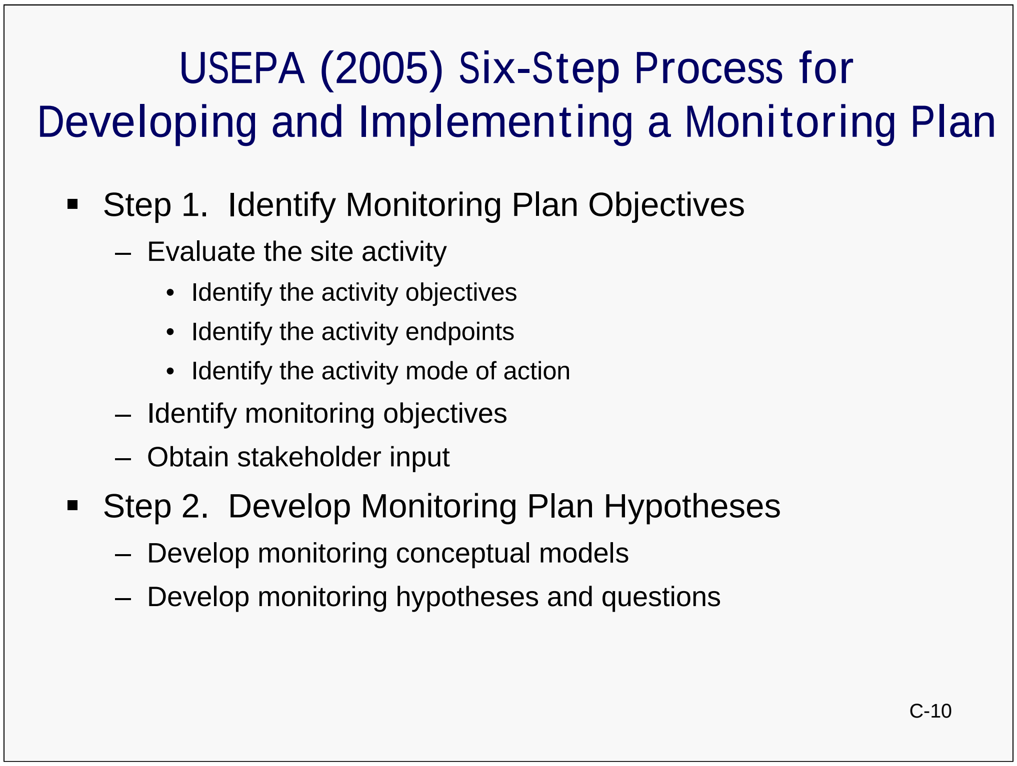
Dredging

- Validate construction and mass removal
- Evaluate surface sediment concentrations
- Validate backfill
- Monitor natural recovery (see MNR)
- Ecological recovery



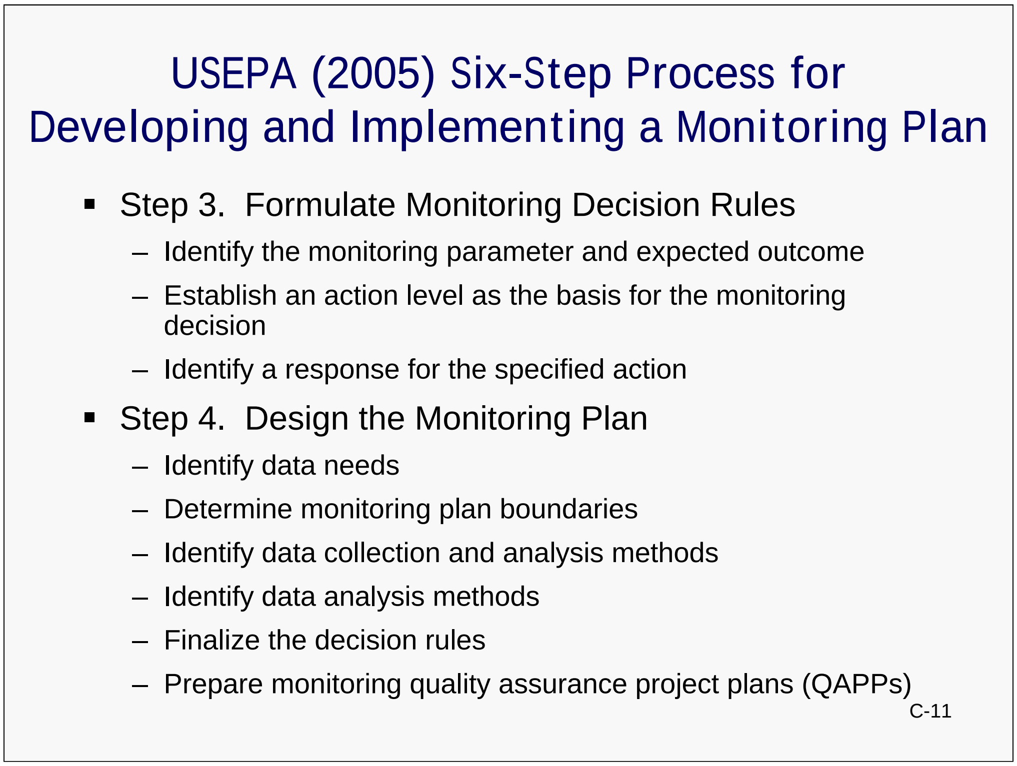
Training Objectives

1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
   - MNR
   - Capping
   - Dredging
3. Present EPA’s six-step monitoring DQO process
4. Identify monitoring tools
5. Wyckoff/Eagle Harbor case study
6. Summary



USEPA (2005) Six-Step Process for Developing and Implementing a Monitoring Plan

- Step 1. Identify Monitoring Plan Objectives
  - Evaluate the site activity
    - Identify the activity objectives
    - Identify the activity endpoints
    - Identify the activity mode of action
  - Identify monitoring objectives
  - Obtain stakeholder input
- Step 2. Develop Monitoring Plan Hypotheses
  - Develop monitoring conceptual models
  - Develop monitoring hypotheses and questions

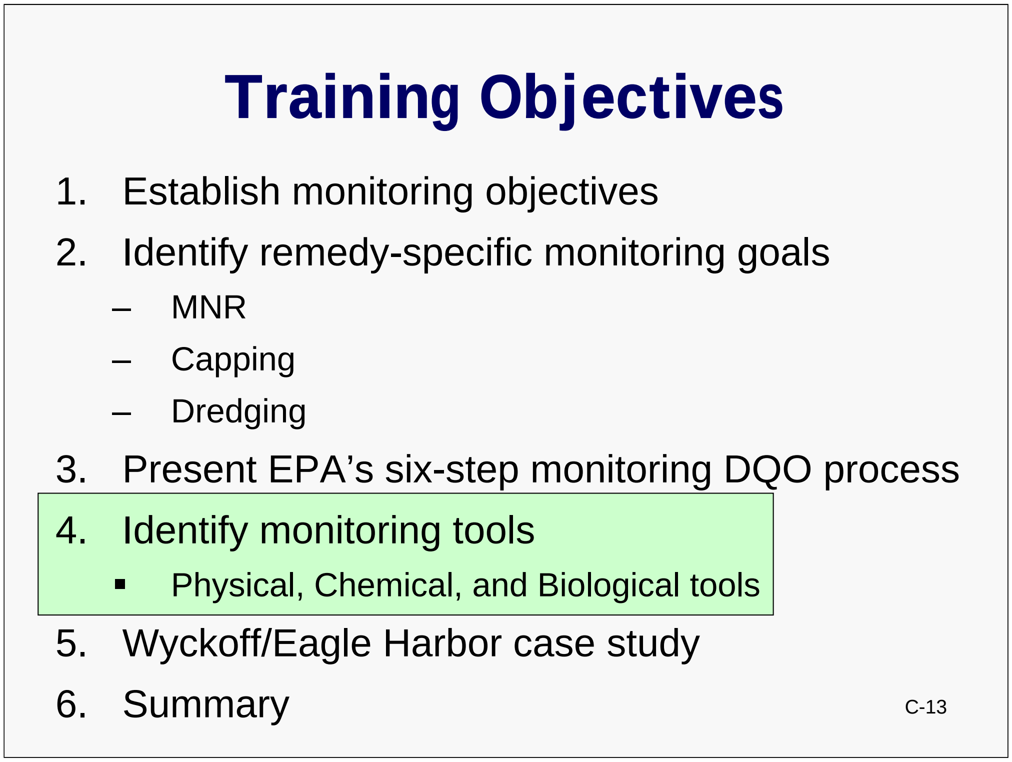


USEPA (2005) Six-Step Process for Developing and Implementing a Monitoring Plan

- Step 3. Formulate Monitoring Decision Rules
  - Identify the monitoring parameter and expected outcome
  - Establish an action level as the basis for the monitoring decision
  - Identify a response for the specified action
- Step 4. Design the Monitoring Plan
  - Identify data needs
  - Determine monitoring plan boundaries
  - Identify data collection and analysis methods
  - Identify data analysis methods
  - Finalize the decision rules
  - Prepare monitoring quality assurance project plans (QAPPs)

USEPA (2005) Six-Step Process for Developing and Implementing a Monitoring Plan

- Step 5. Conduct Monitoring and Characterize Results
  - Conduct data collection and analysis
  - Evaluate results per the monitoring DQOs
  - Revise data collection and analysis as necessary
  - Characterize analytical results and evaluate against decision rules
- Step 6. Establish the Management Decision
  - Conclude monitoring if results support the decision rule for remedy success
  - Continue remedy and monitoring if results do not support the decision rule for remedy success but trend toward supporting remedy success
  - Re-assess uncertainty, revised site activity, or continue monitoring if results do not support the decision rule for remedy success and do not trend toward supporting remedy success



Training Objectives

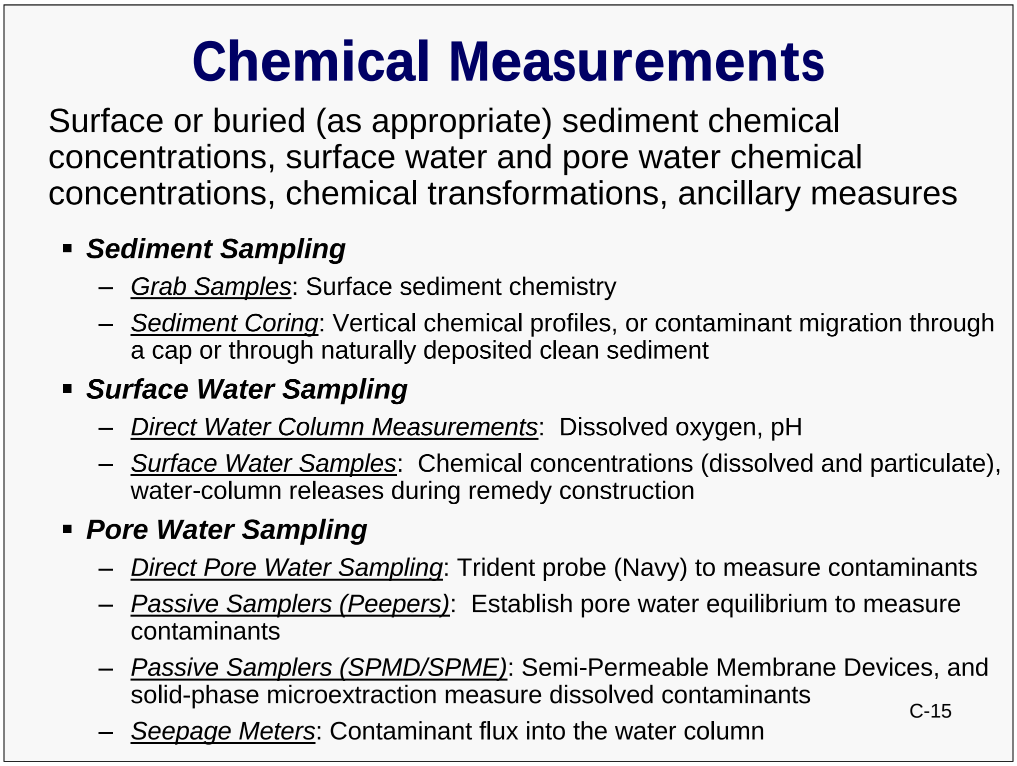
1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
   - MNR
   - Capping
   - Dredging
3. Present EPA’s six-step monitoring DQO process
4. Identify monitoring tools
   - Physical, Chemical, and Biological tools
5. Wyckoff/Eagle Harbor case study
6. Summary

Physical Measurements

Sediment erosion/deposition, ground water and surface water flow rates, and sediment physical characteristics (e.g., particle size, heterogeneity, bulk density)

- ***Sediment Physical Properties***: Fate and transport modeling, sediment characteristics, post-remedy surface sediment features
- ***Water Column Physical Measurements (e.g., turbidity, suspended solids)***: Sediment suspension during remedy implementation
- ***Bathymetry***: Evaluate pre-remedy and post-remedy bottom elevations
- ***Side Scan Sonar Data***: Monitor sediment types and bedforms
- ***Settlement Plate Data***: Changes in cap thickness, cap consolidation
- ***Sediment Profile Camera Data***: Visual surface sediment characteristics, bioturbation/oxidation depths, presence of gas bubbles
- ***Subbottom Profiler Data***: Changes in sediment surface and subsurface composition, presence of gas bubbles

C-14



Chemical Measurements

Surface or buried (as appropriate) sediment chemical concentrations, surface water and pore water chemical concentrations, chemical transformations, ancillary measures

- ***Sediment Sampling***
  - *Grab Samples*: Surface sediment chemistry
  - *Sediment Coring*: Vertical chemical profiles, or contaminant migration through a cap or through naturally deposited clean sediment
- ***Surface Water Sampling***
  - *Direct Water Column Measurements*: Dissolved oxygen, pH
  - *Surface Water Samples*: Chemical concentrations (dissolved and particulate), water-column releases during remedy construction
- ***Pore Water Sampling***
  - *Direct Pore Water Sampling*: Trident probe (Navy) to measure contaminants
  - *Passive Samplers (Peepers)*: Establish pore water equilibrium to measure contaminants
  - *Passive Samplers (SPMD/SPME)*: Semi-Permeable Membrane Devices, and solid-phase microextraction measure dissolved contaminants
  - *Seepage Meters*: Contaminant flux into the water column

Biological Measurements

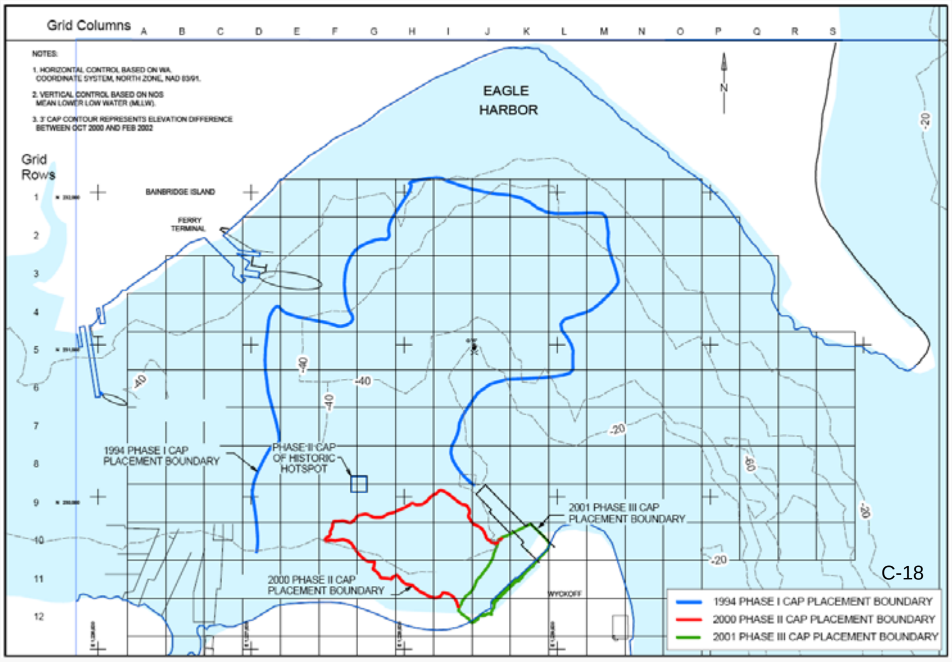
Biological testing can include toxicity assays, assessment of changes in the biological assemblages at sites, or toxicant bioaccumulation and food chain effects.

- ***Benthic Community Analysis***: Evaluate population size, density, and diversity, and monitor recovery
- ***Toxicity Testing***: Measure acute and long-term lethal or sub-lethal contaminant effects on organisms
- ***Tissue Sampling***: Measure bioaccumulation, model trophic transfer potential, and estimate food web effects
- ***Caged Fish/Invertebrate Studies***: Monitor changes in contaminant uptake (bioaccumulation rates) by biota in sediment or water column
- ***Sediment Profile Camera Studies***: Characterize macroinvertebrate recolonization, polychaete population density, redox zones, and benthic mixing

Training Objectives

1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
   - MNR
   - Capping
   - Dredging
3. Present EPA's six-step monitoring DQO process
4. Identify monitoring tools
   - Physical, Chemical, and Biological tools
5. Wyckoff/Eagle Harbor case study
6. Summary

Eagle Harbor Cap



C-18

Wyckoff/Eagle Harbor Monitoring Objectives

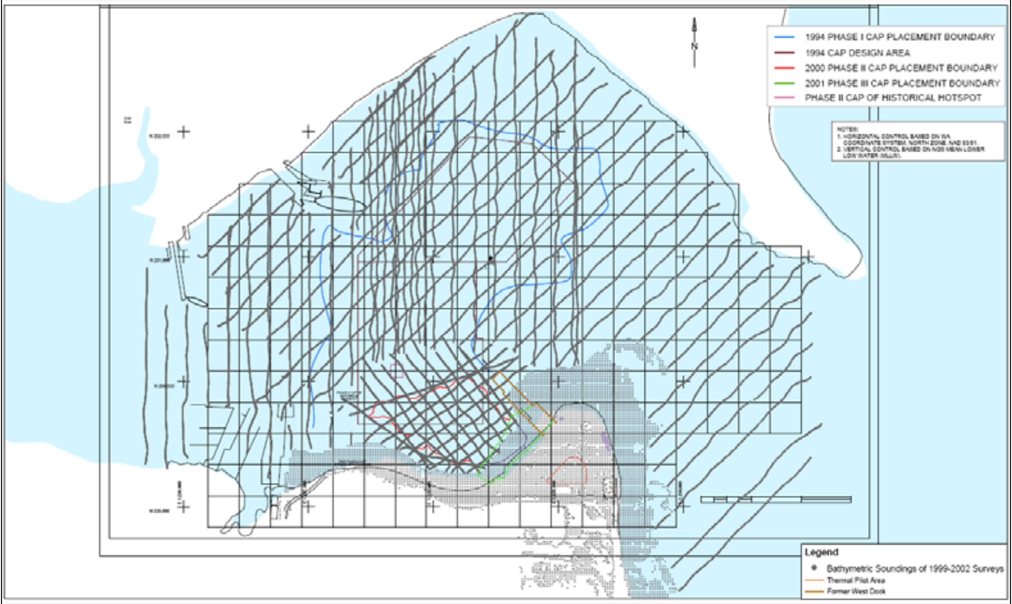
1. Is the cap physically stable, remaining in place at a desired thickness?
2. Is the cap effectively isolating the underlying contaminated sediments?
3. Are sediments in the biologically active zone (0-10 cm) remaining clean relative to the Washington State Sediment Management Standards (SMS)?

Monitoring Tool	Cap Performance Objective Addressed
Bathymetry	Objective 1
Surface sediment chemistry	Objective 3
Through-cap coring and chemistry	Objective 1, Objective 2

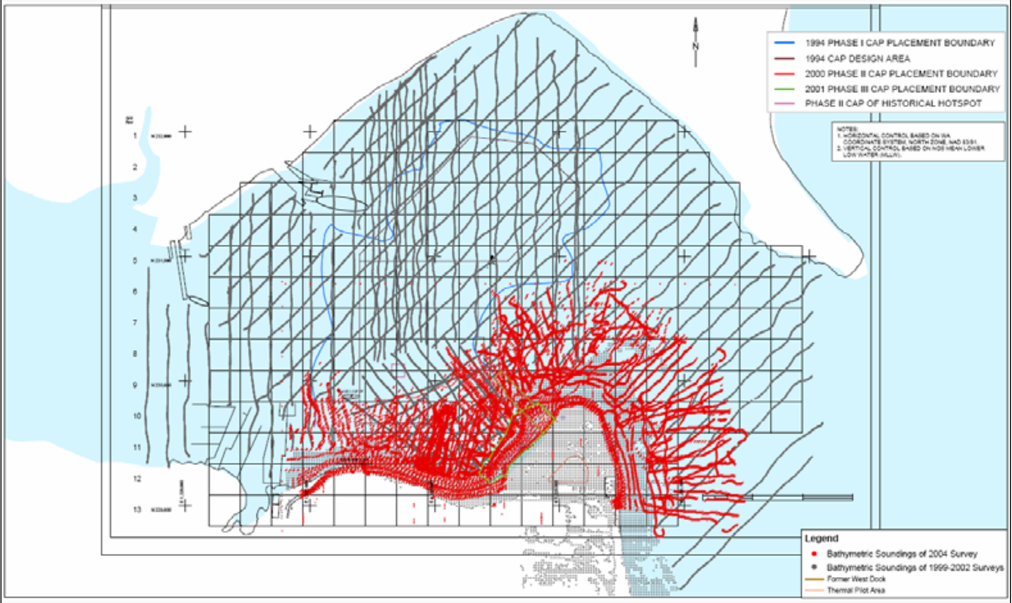
Wyckoff/Eagle Harbor Monitoring Plan

- **Precision Navigation**
  - Integrated navigation provided for all monitoring
  - Positional accuracy of 2 meters
- **Bathymetry**
  - Bathymetric soundings measure differences in seafloor elevations
  - Determine cap thickness after capping, and long-term changes in cap thickness
- **On-Cap Surface Sediment Grabs**
  - Surface sediment samples (0-10 cm) collected from 15 stations
  - Analyzed for PAH to evaluate the chemical character of cap surface
- **Off-Cap Surface Sediment Grabs**
  - Surface sediment samples (0-10 cm) collected from 1 station
  - Analyzed for PAH to characterize and monitor off-cap subtidal and intertidal areas
- **Through-Cap Coring**
  - Core samples of the cap were collected at 9 stations
  - Analyzed the 15-30 cm portion of cap overlying contaminated native sediment
  - Analyze for PAH to evaluate upward contamination migration through cap
  - Archive remaining core portions

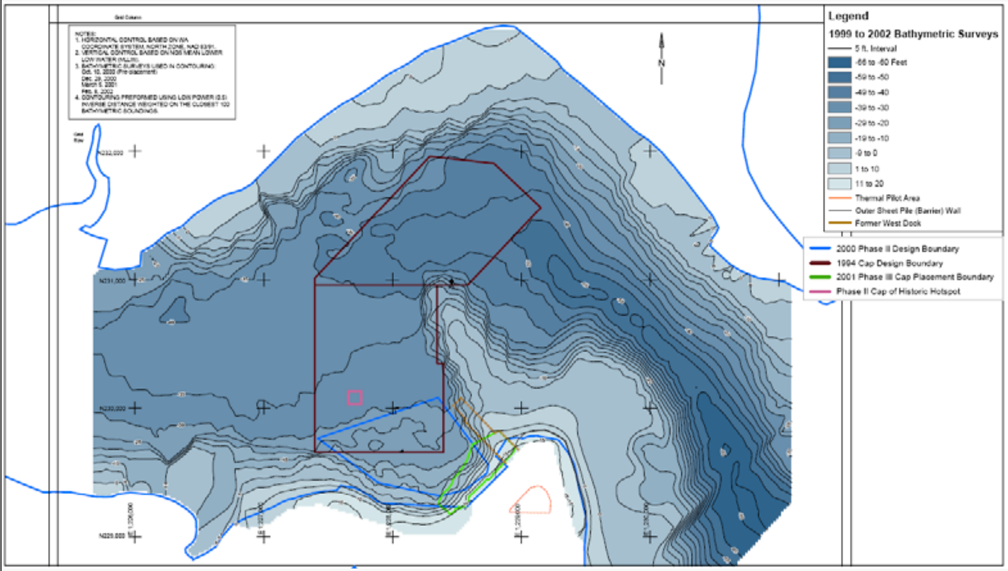
1999-2002 Bathymetric Transects



2002-2004 Bathymetric Transects

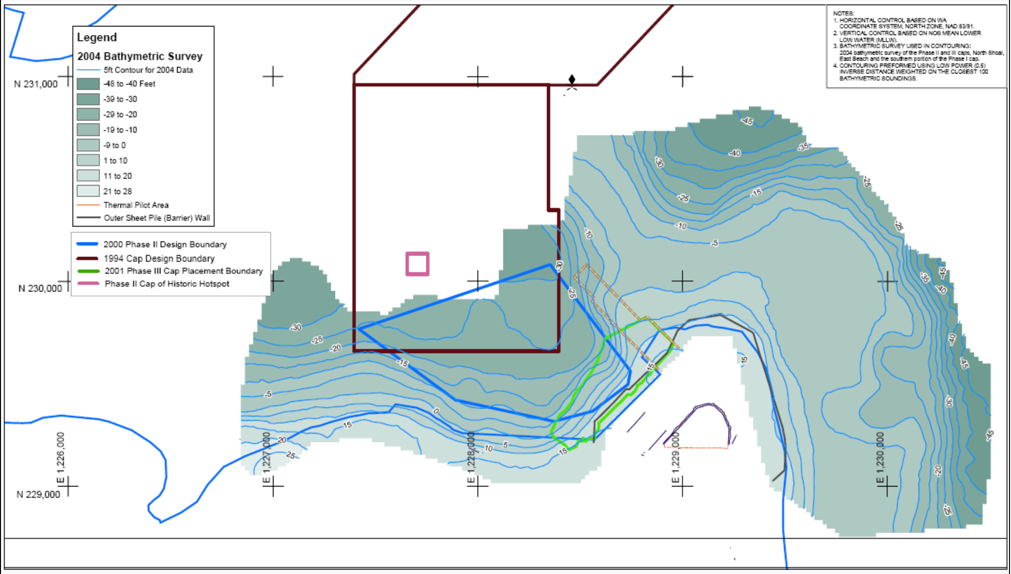


1999 to 2002 Bathymetric Surveys



C-23

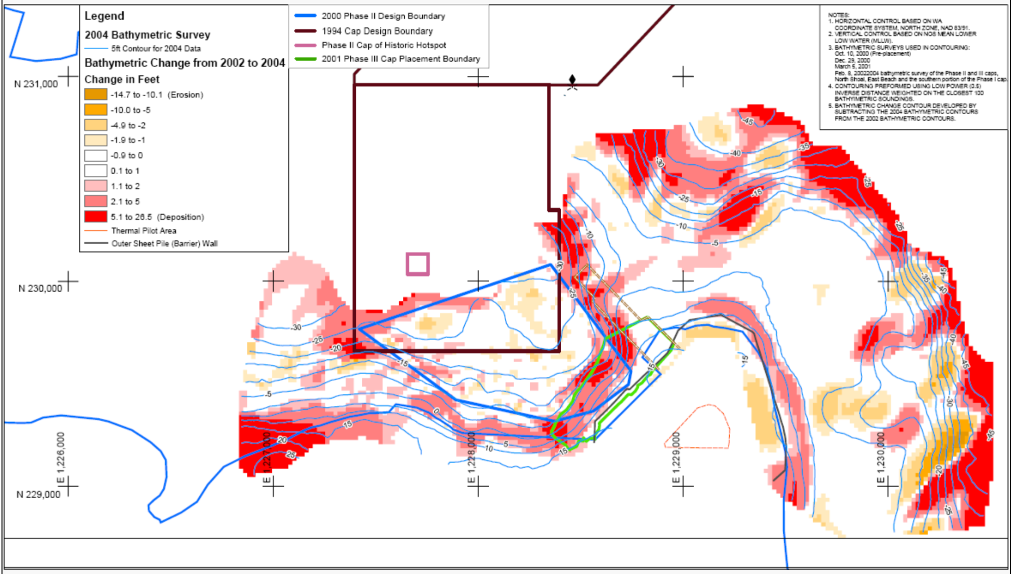
2004 Bathymetric Survey



NOTES:
1. HORIZONTAL CONTROL BASED ON WA COORDINATE SYSTEM, NORTH ZONE, NAD 83/91.
2. VERTICAL CONTROL BASED ON NOS MEAN LOWER LOW WATER (MLLW).
3. BATHYMETRIC SURVEY USED IN CONTOURING: 2004 bathymetric survey of the Phase II and III caps, North Shoal, East Beach and the southern portion of the Phase I cap.
4. CONTOURING PREFORMED USING LOW POWER (0.5) INVERSE DISTANCE WEIGHTED ON THE CLOSEST 100 BATHYMETRIC SOUNDINGS.

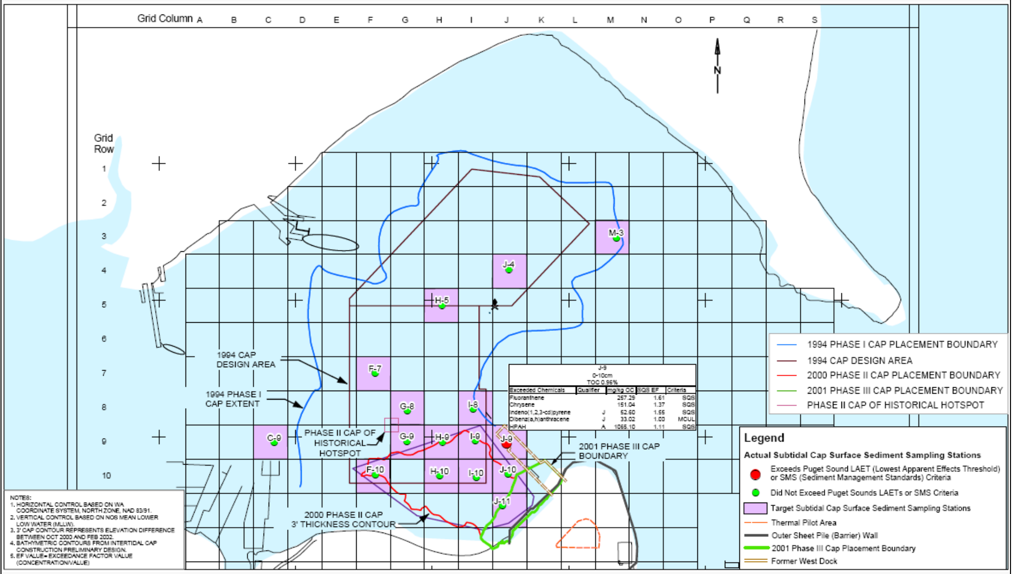
C-24

Bathymetric Change: 2002 to 2004



NOTES:
1. HORIZONTAL CONTROL BASED ON WA COORDINATE SYSTEM, NORTH ZONE, NAD 83/91.
2. VERTICAL CONTROL BASED ON NOS MEAN LOWER LOW WATER (MLLW).
3. BATHYMETRIC SURVEYS USED IN CONTOURING:
   Oct. 10, 2000 (Pre-placement)
   Dec. 29, 2000
   March 5, 2001
   Feb. 8, 20022004 bathymetric survey of the Phase II and III caps, North Shoal, East Beach and the southern portion of the Phase I cap.
4. CONTOURING PREFORMED USING LOW POWER (0.5) INVERSE DISTANCE WEIGHTED ON THE CLOSEST 100 BATHYIMETRIC SOUNDINGS.
5. BATHYMETRIC CHANGE CONTOUR DEVELOPED BY SUBTRACTING THE 2004 BATHYMETRIC CONTOURS FROM THE 2002 BATHYMETRIC CONTOURS.

Subtidal Cap Surface Sampling



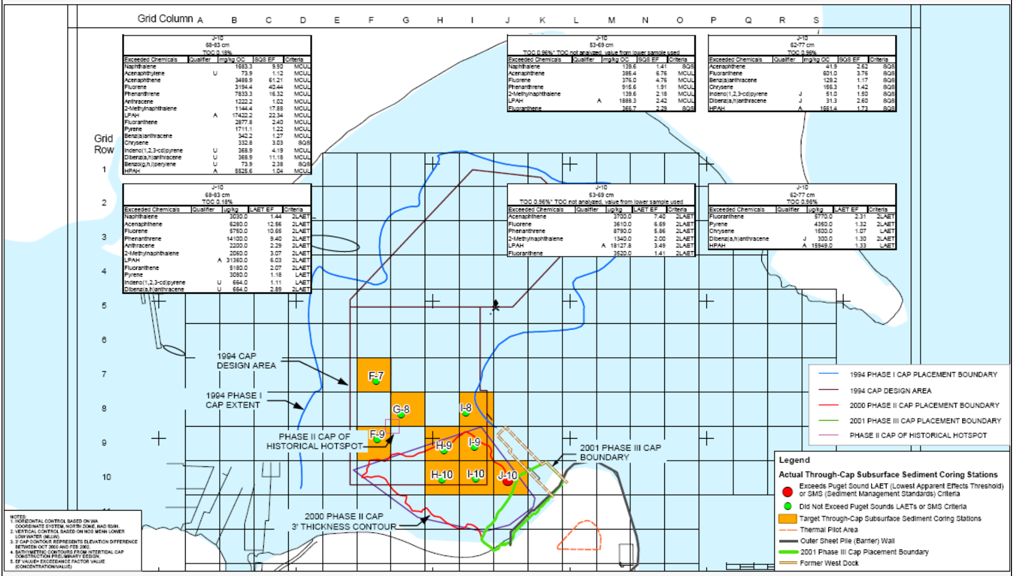
J-9
0-10cm
TOC 0.96%

Exceeded Chemicals	Qualifier	mg/kg OC	SQS EF	Criteria
Fluoranthene		257.29	1.61	SQS
Chrysene		151.04	1.37	SQS
Indeno(1,2,3-cd)pyrene	J	52.60	1.55	SQS
Dibenz(a,h)anthracene	J	33.02	1.00	MCUL
HPAH	A	1065.10	1.11	SQS

NOTES:
1. HORIZONTAL CONTROL BASED ON WA COORDINATE SYSTEM, NORTH ZONE, NAD 83/91.
2. VERTICAL CONTROL BASED ON NOS MEAN LOWER LOW WATER (MLLW).
3. 3' CAP CONTOUR REPRESENTS ELEVATION DIFFERENCE BETWEEN OCT 2000 AND FEB 2002.
4. BATHYMETRIC CONTOURS FROM INTERTIDAL CAP CONSTRUCTION PRELIMINARY DESIGN.
5. EF VALUE= EXCEEDANCE FACTOR VALUE (CONCENTRATION/VALUE)

C-26

Through-Cap Subtidal Sediment Coring Results



J-10
68-83 cm
TOC 0.18%

Exceeded Chemicals	Qualifier	mg/kg OC	SQS EF	Criteria
Naphthalene		1683.3	9.90	MCUL
Acenaphthylene	U	73.9	1.12	MCUL
Acenaphthene		3488.9	61.21	MCUL
Fluorene		3194.4	40.44	MCUL
Phenanthrene		7833.3	16.32	MCUL
Anthracene		1222.2	1.02	MCUL
2-Methylnaphthalene		1144.4	17.88	MCUL
LPAH	A	17422.2	22.34	MCUL
Fluoranthene		2877.8	2.40	MCUL
Pyrene		1711.1	1.22	MCUL
Benz(a)anthracene		342.2	1.27	MCUL
Chrysene		332.8	3.03	SQS
Indeno(1,2,3-cd)pyrene	U	368.9	4.19	MCUL
Dibenz(a,h)anthracene	U	368.9	11.18	MCUL
Benzo(g,h,i)perylene	U	73.9	2.38	SQS
HPAH	A	5525.6	1.04	MCUL

J-10
68-83 cm
TOC 0.18%

Exceeded Chemicals	Qualifier	µg/kg	LAET EF	Criteria
Naphthalene		3030.0	1.44	2LAET
Acenaphthene		6280.0	12.56	2LAET
Fluorene		5750.0	10.65	2LAET
Phenanthrene		14100.0	9.40	2LAET
Anthracene		2200.0	2.29	2LAET
2-Methylnaphthalene		2060.0	3.07	2LAET
LPAH	A	31360.0	6.03	2LAET
Fluoranthene		5180.0	2.07	2LAET
Pyrene		3080.0	1.18	LAET
Indeno(1,2,3-cd)pyrene	U	664.0	1.11	LAET
Dibenz(a,h)anthracene	U	664.0	2.89	2LAET

J-10
53-69 cm
TOC 0.96%* TOC not analyzed, value from lower sample used

Exceeded Chemicals	Qualifier	mg/kg OC	SQS EF	Criteria
Naphthalene		139.6	1.41	SQS
Acenaphthene		385.4	6.76	MCUL
Fluorene		376.0	4.76	MCUL
Phenanthrene		915.6	1.91	MCUL
2-Methylnaphthalene		139.6	2.18	MCUL
LPAH	A	1888.3	2.42	MCUL
Fluoranthene		366.7	2.29	SQS

J-10
53-69 cm
TOC 0.96%* TOC not analyzed, value from lower sample used

Exceeded Chemicals	Qualifier	µg/kg	LAET EF	Criteria
Acenaphthene		3700.0	7.40	2LAET
Fluorene		3610.0	6.69	2LAET
Phenanthrene		8790.0	5.86	2LAET
2-Methylnaphthalene		1340.0	2.00	2LAET
LPAH	A	18127.8	3.49	2LAET
Fluoranthene		3520.0	1.41	2LAET

J-10
62-77 cm
TOC 0.96%

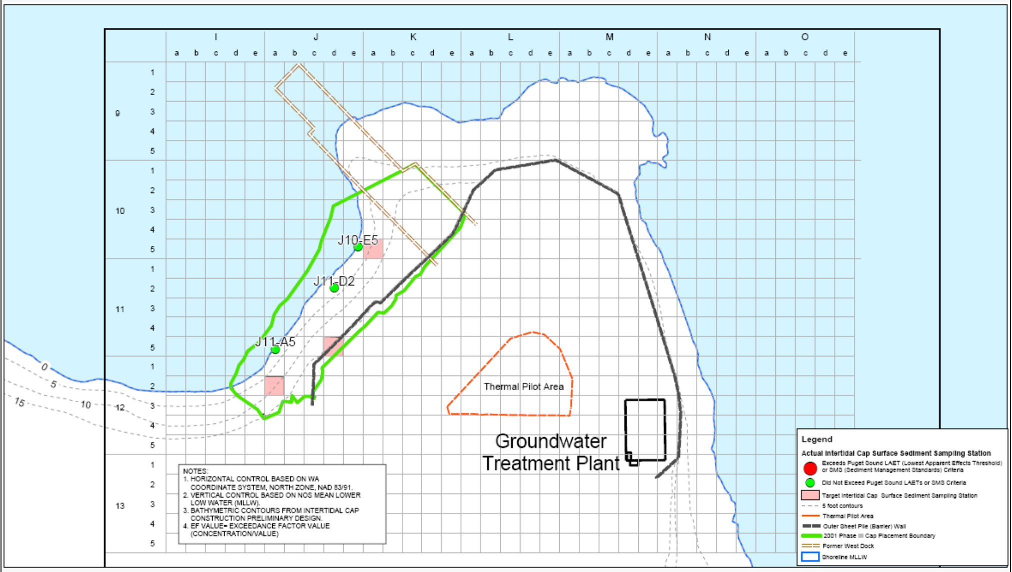
Exceeded Chemicals	Qualifier	mg/kg OC	SQS EF	Criteria
Acenaphthene		41.9	2.62	SQS
Fluoranthene		601.0	3.76	SQS
Benz(a)anthracene		129.2	1.17	SQS
Chrysene		156.3	1.42	SQS
Indeno(1,2,3-cd)pyrene	J	51.0	1.50	SQS
Dibenz(a,h)anthracene	J	31.3	2.60	SQS
HPAH	A	1661.4	1.73	SQS

J-10
62-77 cm
TOC 0.96%

Exceeded Chemicals	Qualifier	µg/kg	LAET EF	Criteria
Fluoranthene		5770.0	2.31	2LAET
Pyrene		4350.0	1.32	2LAET
Chrysene		1500.0	1.07	LAET
Dibenz(a,h)anthracene	J	300.0	1.30	2LAET
HPAH	A	15949.0	1.33	LAET

NOTES:
1. HORIZONTAL CONTROL BASED ON WA COORDINATE SYSTEM, NORTH ZONE, NAD 83/91.
2. VERTICAL CONTROL BASED ON NOS MEAN LOWER LOW WATER (MLLW).
3. 3' CAP CONTOUR REPRESENTS ELEVATION DIFFERENCE BETWEEN OCT 2000 AND FEB 2002.
4. BATHYMETRIC CONTOURS FROM INTERTIDAL CAP CONSTRUCTION PRELIMINARY DESIGN.
5. EF VALUE= EXCEEDANCE FACTOR VALUE (CONCENTRATION/VALUE)

Intertidal Sediment Surface Sampling



NOTES:
1. HORIZONTAL CONTROL BASED ON WA COORDINATE SYSTEM, NORTH ZONE, NAD 83/91.
2. VERTICAL CONTROL BASED ON NOS MEAN LOWER LOW WATER (MLLW).
3. BATHYMETRIC CONTOURS FROM INTERTIDAL CAP CONSTRUCTION PRELIMINARY DESIGN.
4. EF VALUE= EXCEEDANCE FACTOR VALUE (CONCENTRATION/VALUE)

Legend

Actual Intertidal Cap Surface Sediment Sampling Station

- 🔴 Exceeds Puget Sound LAET (Lowest Apparent Effects Threshold) or SMS (Sediment Management Standards) Criteria
- 🟢 Did Not Exceed Puget Sound LAETs or SMS Criteria
- 🟥 Target Intertidal Cap Surface Sediment Sampling Station
- - - 5 foot contours
- — Thermal Pilot Area
- ▬ ▬ Outer Sheet Pile (Barrier) Wall
- ▬ 2001 Phase III Cap Placement Boundary
- ═ ═ Former West Dock
- ☐ Shoreline MLLW

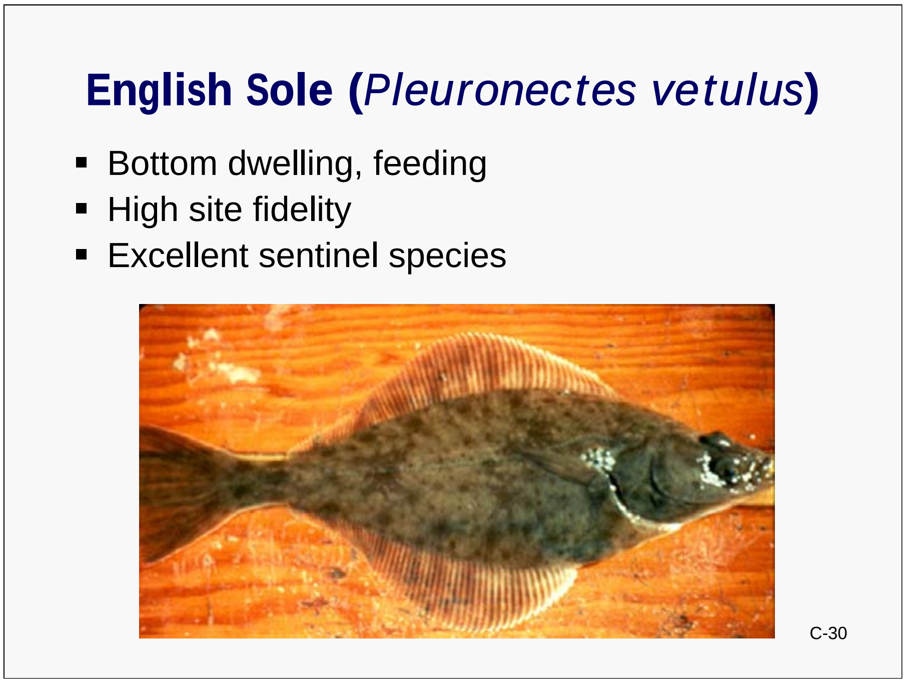
Improvement in English Sole Health After Sediment Capping at Eagle Harbor

For more information, contact:

M.S. Myers, B.F. Anulacion, B.L. French, C.A. Laetz, W.D. Reichert, J.L. Buzitis, and T.K. Collier

Environmental Conservation Division
Northwest Fisheries Science Center
National Marine Fisheries Service

Seattle, WA   USA

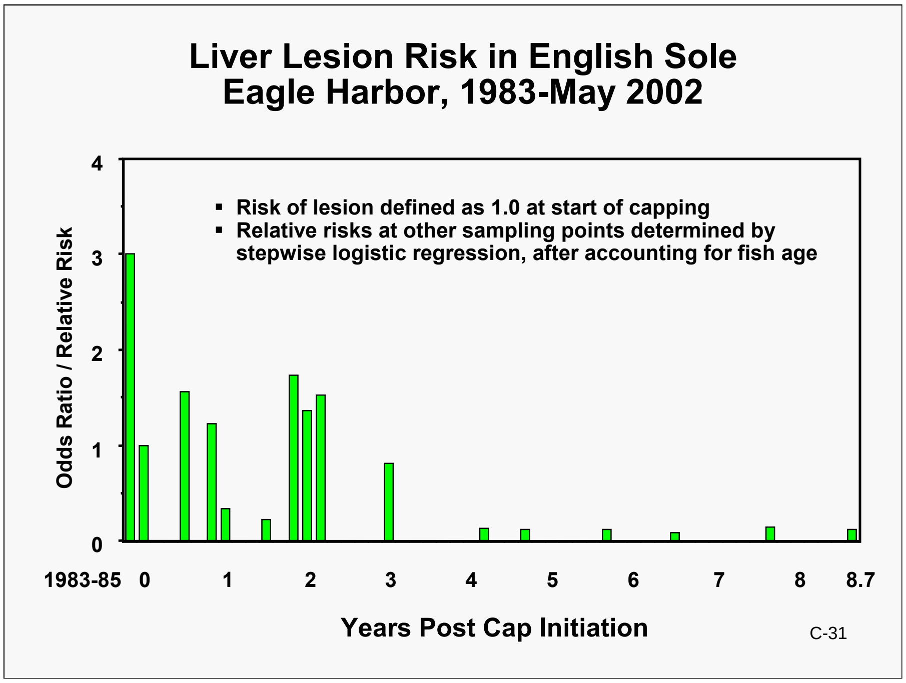


English Sole (*Pleuronectes vetulus*)

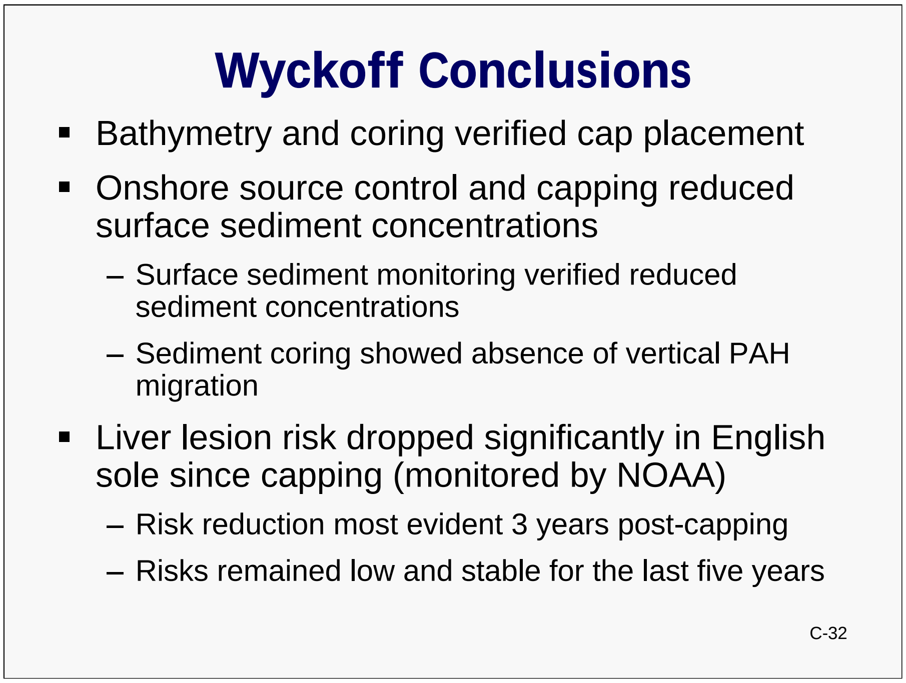
- Bottom dwelling, feeding
- High site fidelity
- Excellent sentinel species

C-30

Using English sole as our chosen sentinel species, also found high levels of PAH metabolites in bile, PAHs in stomach contents (84,000 ppb)

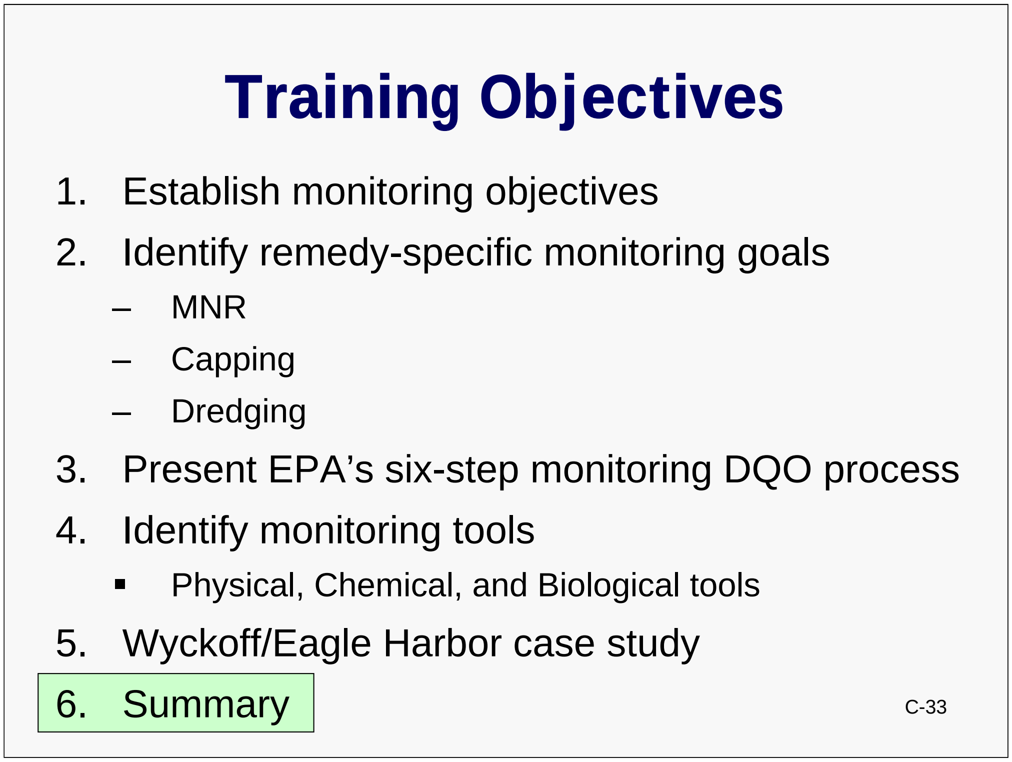


Perhaps the most dramatic changes have been in risk of toxicopathic liver lesions. If we define the baseline risk at the start of capping as 1.0, the relative risk in ‘83-85 was almost 3x the baseline risk. After adjusting for influence of age on risk of lesion occurrence, relative risks up to 3 years after capping were highly variable. But from year 4 after capping to the latest sampling in May ‘02, the relative risks have been very low, in the vicinity of 0.1 (corr. to ~2-4% prevalence).



Wyckoff Conclusions

- Bathymetry and coring verified cap placement
- Onshore source control and capping reduced surface sediment concentrations
  - Surface sediment monitoring verified reduced sediment concentrations
  - Sediment coring showed absence of vertical PAH migration
- Liver lesion risk dropped significantly in English sole since capping (monitored by NOAA)
  - Risk reduction most evident 3 years post-capping
  - Risks remained low and stable for the last five years

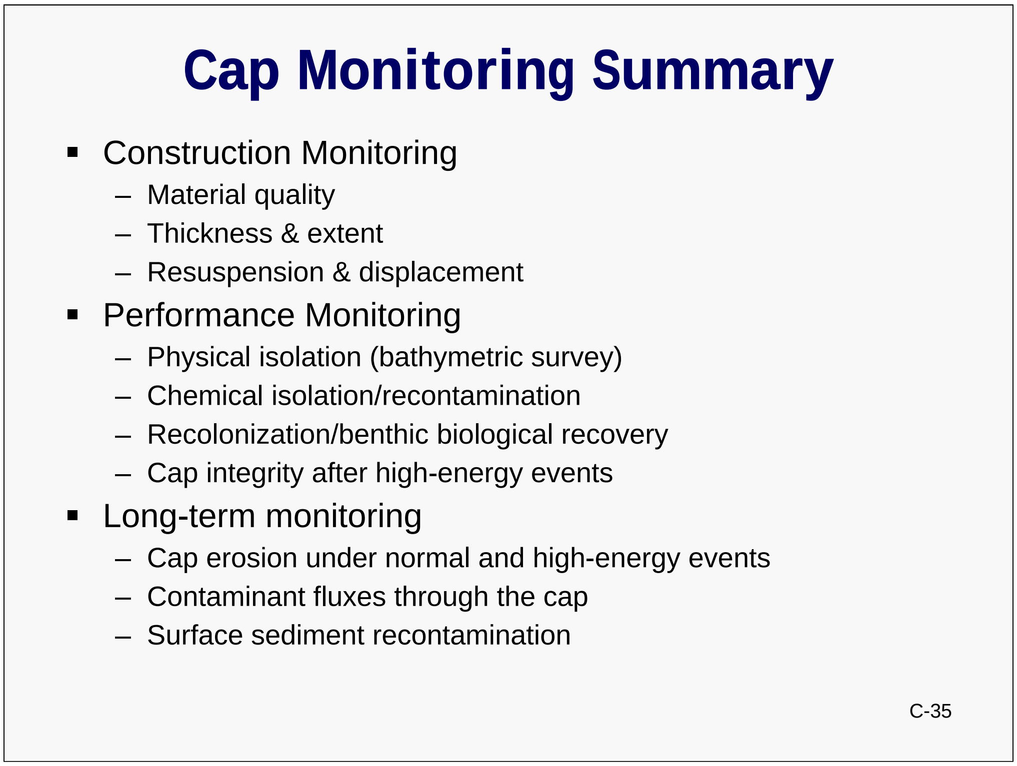


Training Objectives

1. Establish monitoring objectives
2. Identify remedy-specific monitoring goals
    - MNR
    - Capping
    - Dredging
3. Present EPA’s six-step monitoring DQO process
4. Identify monitoring tools
    - Physical, Chemical, and Biological tools
5. Wyckoff/Eagle Harbor case study
6. Summary

MNR Monitoring Summary

- Validate CSM and numerical model predictions
- Monitor direct or indirect measures of natural processes
  - Sediment accumulation
  - Degradation products
  - Sediment and contaminant transport
- Monitor environmental contaminant levels
  - Surface sediment
  - Surface water
  - Surface-sediment pore water
- Monitor ecological recovery
  - Sediment contaminant toxicity
  - Biological community health, density, diversity
  - Contaminant bioaccumulation
  - Higher food-chain ecological receptors
- Sediment stability under normal and high-energy events



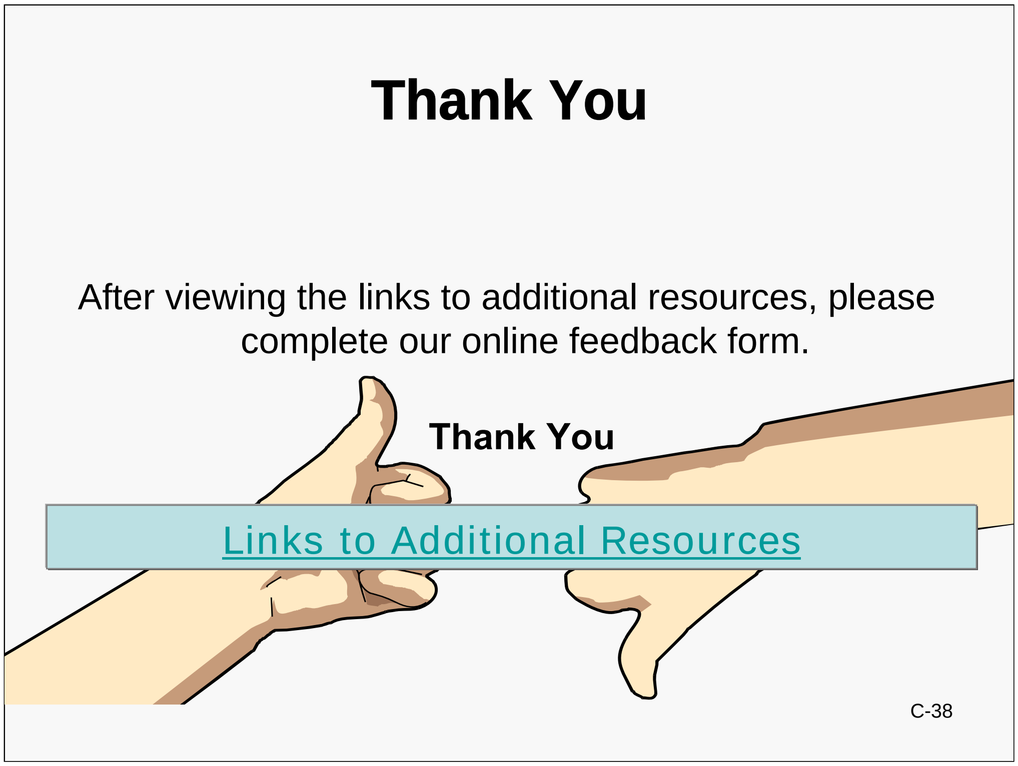
Cap Monitoring Summary

- Construction Monitoring
  - Material quality
  - Thickness & extent
  - Resuspension & displacement
- Performance Monitoring
  - Physical isolation (bathymetric survey)
  - Chemical isolation/recontamination
  - Recolonization/benthic biological recovery
  - Cap integrity after high-energy events
- Long-term monitoring
  - Cap erosion under normal and high-energy events
  - Contaminant fluxes through the cap
  - Surface sediment recontamination

Dredge/Excavation Monitoring Summary

- Dredge Compliance Monitoring
  - Residual contaminant concentrations
  - Dredge excavation depths
  - Dredge throughput volumes
- Construction performance monitoring
  - Near-field and far-field surface water
  - Dewatering and water treatment performance
  - Acute toxicity biological monitoring (e.g., caged fish or mussels)
  - Transport/dewatering/pretreatment
  - Air monitoring
  - On-site treatment and disposal operations
- Long-term monitoring
  - Surface sediment contaminant concentrations
  - Benthic community recovery
  - Tissue concentrations in fish or shellfish

C-37



Thank You

After viewing the links to additional resources, please complete our online feedback form.

[Links to Additional Resources]