

# GSI Can Affect the Bioavailability of Sediment-Associated Contaminants to Benthic Invertebrates

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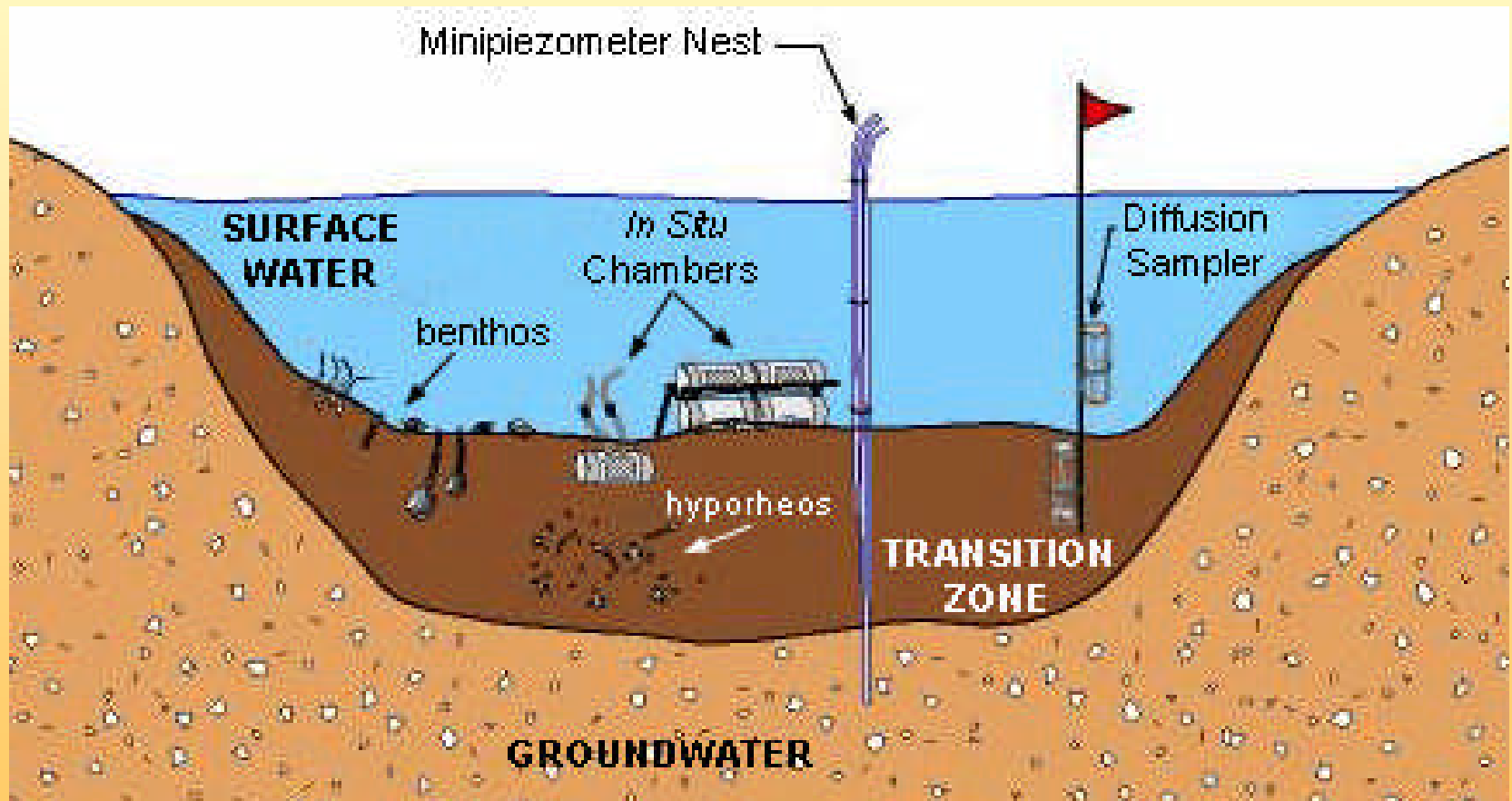
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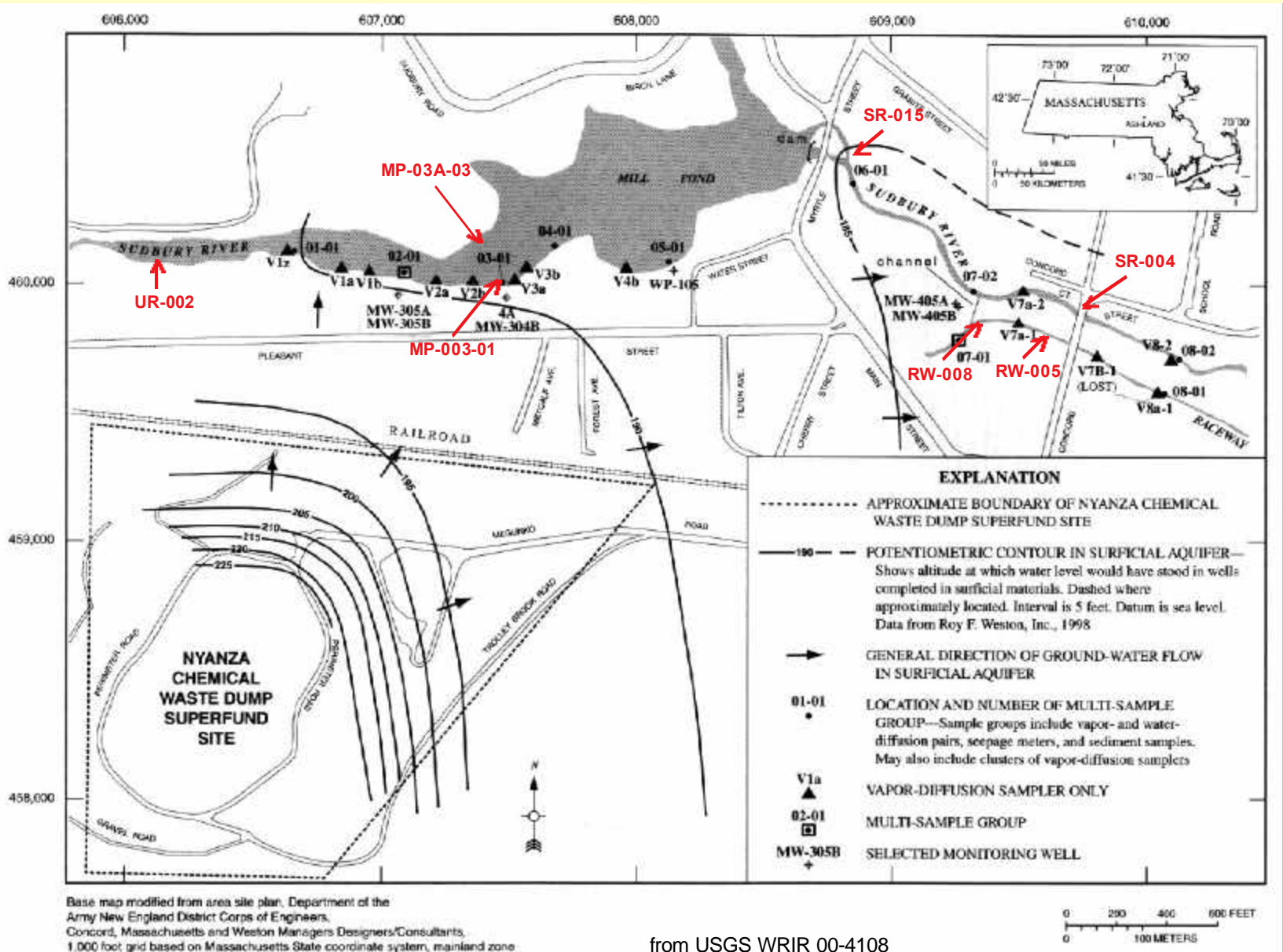
# Sediment Toxicity Assessment and GW-SW Interactions

- GW-SW interactions in relation to sediment toxicity important in ecological risk assessment
- GSI issues exist at numerous contaminated sites:
  - 75% all RCRA/Superfund w/in 1/2 mile of surface water
  - 51% NPL sites with surface water contaminated (most via groundwater transport)
  - observed at many sites we have studied

# Integrated *In Situ* Assessment Design



# Nyanza - Sudbury River System



# Hydrological Measurements - Sudbury River - Nyanza Study

| Site                   | Hydrological Conditions <sup>a</sup> | $\Delta h$ (cm) Range | VHG (cm/cm) Range |
|------------------------|--------------------------------------|-----------------------|-------------------|
| UR-002                 | Upwelling                            | 0.2 – 0.9             | 0.004 – 0.060     |
| MP-03A-03              | Upwelling                            | 0.2 – 10.3            | 0.013 – 0.137     |
| MP-003-01 <sup>b</sup> | Mixed Up/Down                        | -0.2 – 9.70           | -0.006 – 0.129    |
| SR-015                 | Upwelling                            | 0.3 – 0.7             | 0.007 – 0.013     |
| SR-004                 | Upwelling                            | 0.4 – 7.0             | 0.011 - 0.093     |
| RW-008                 | Upwelling                            | 0.4 – 3.8             | 0.011 – 0.051     |
| RW-005                 | Upwelling                            | 0.5 – 1.7             | 0.009 – 0.053     |

<sup>a</sup> Determined from manometer readings of two nested mini-piezometers (20, 40, 60 and 80 cm depths)

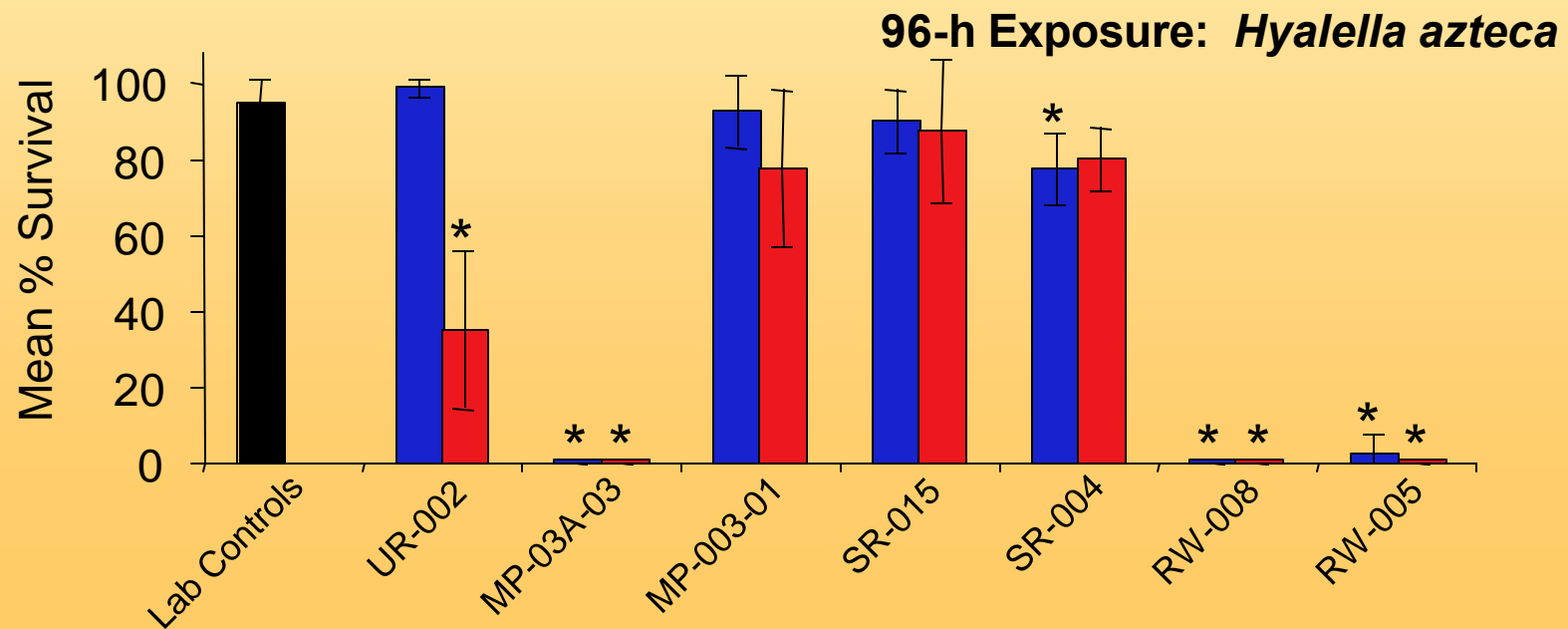
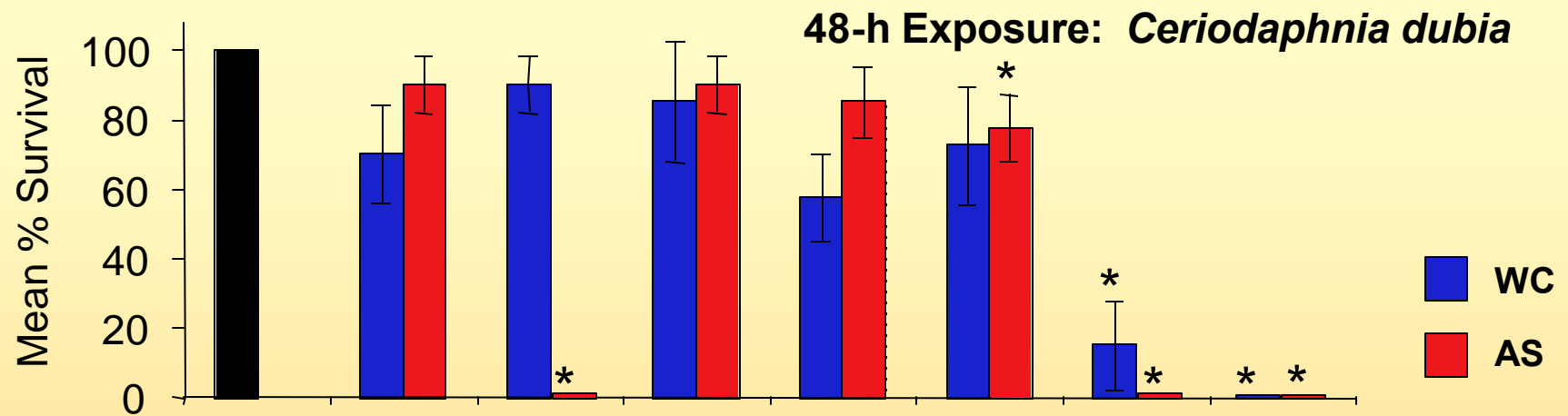
<sup>b</sup> Deep water site

# Chemistry - Nyanza Study

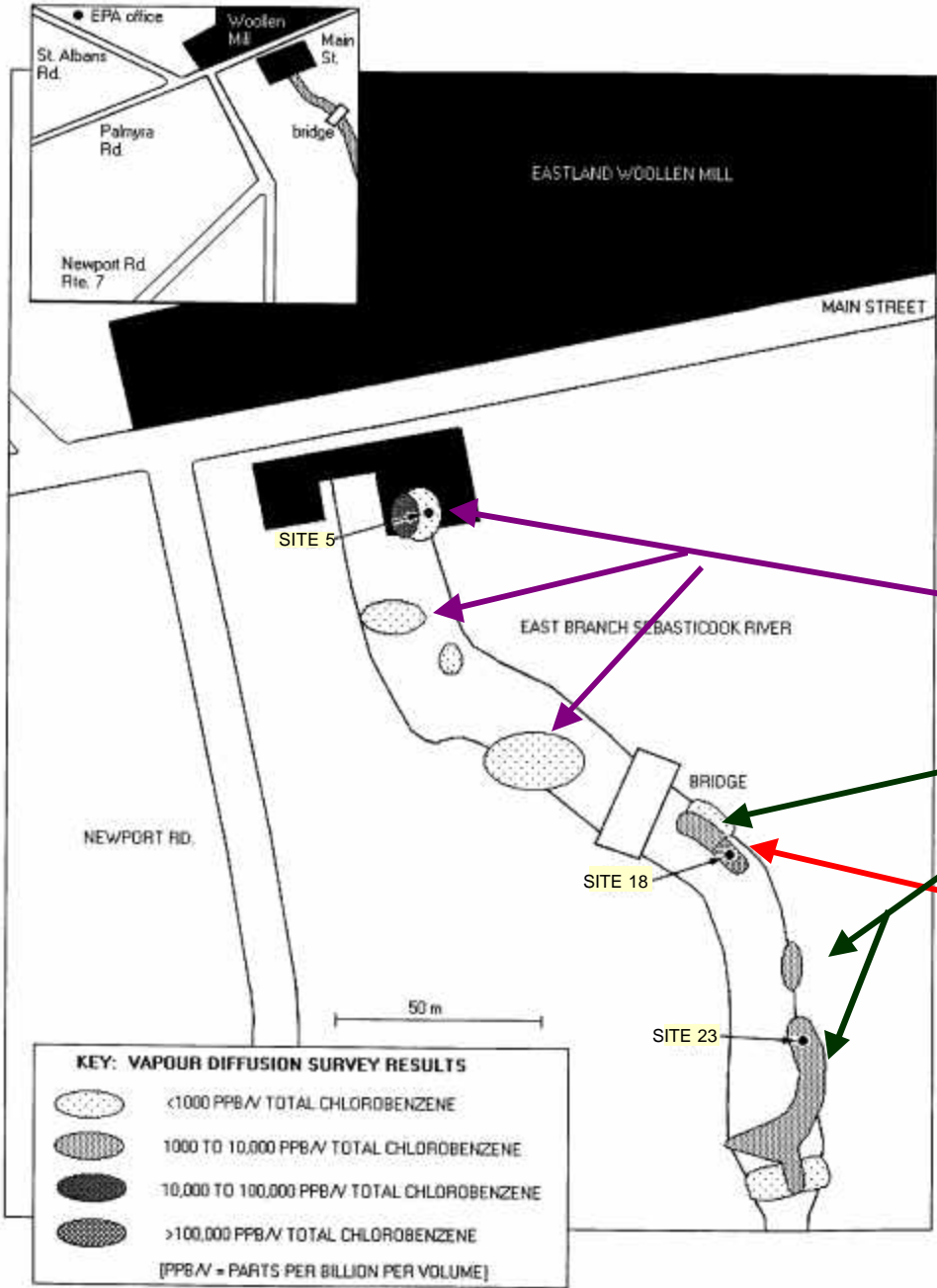
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- Metals (incl. Ag, As, Cd, Cu, Hg, Ni, Pb, Zn) exceeded WQC in groundwater at all 7 sites and SQGs in sediments at 6 sites
- VOCs exceeded criteria in the groundwater at 3 sites and in the sediments at 4 sites
- Most exceedances in the Mill Pond and Raceway sites
- Contaminants detected in samples from chamber waters reflected groundwater and sediments

# *In Situ* Exposure Nyanza Study



# Eastland Woolen Mill Corinna, ME



Total chlorobenzene  
(vapor diffusion)

<1000 ppb/v

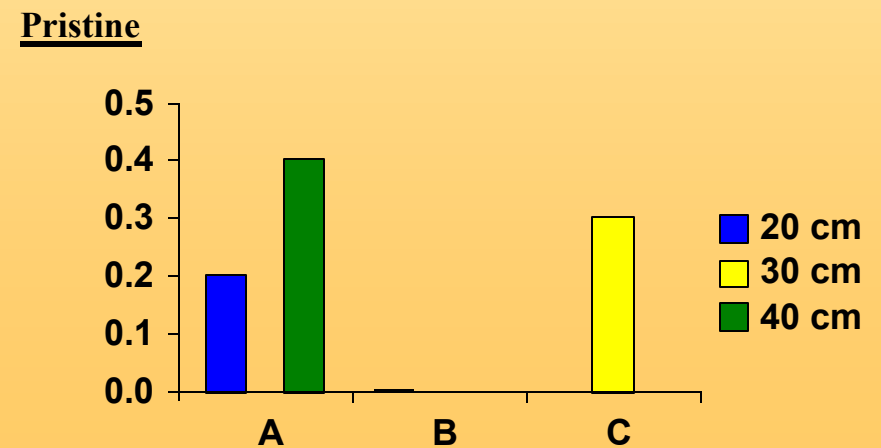
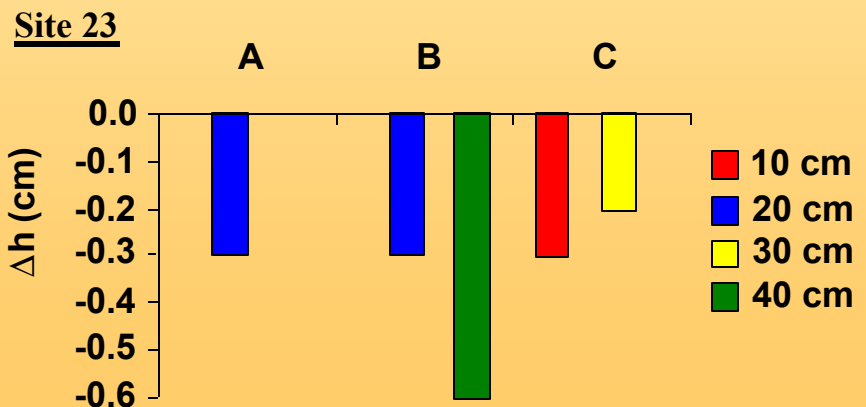
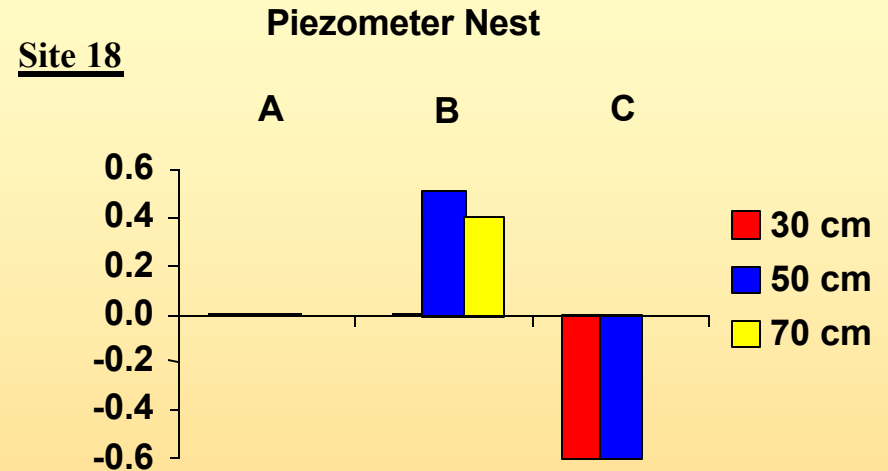
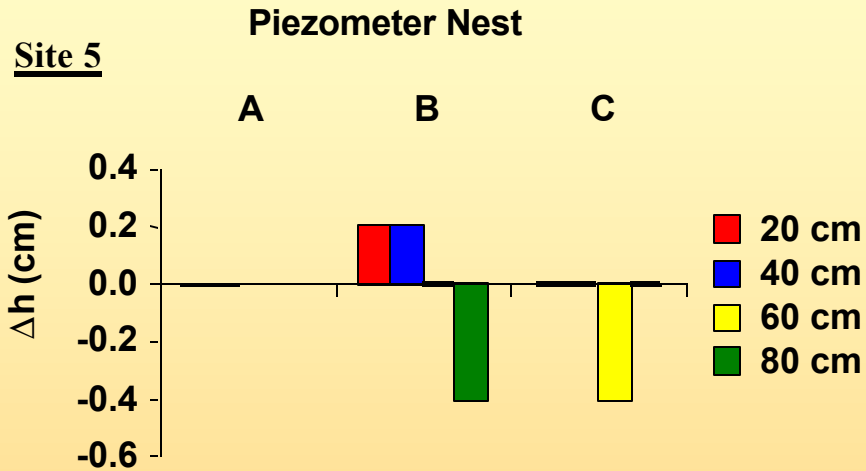
1000 -> 10,000

10,000 -> 100,000

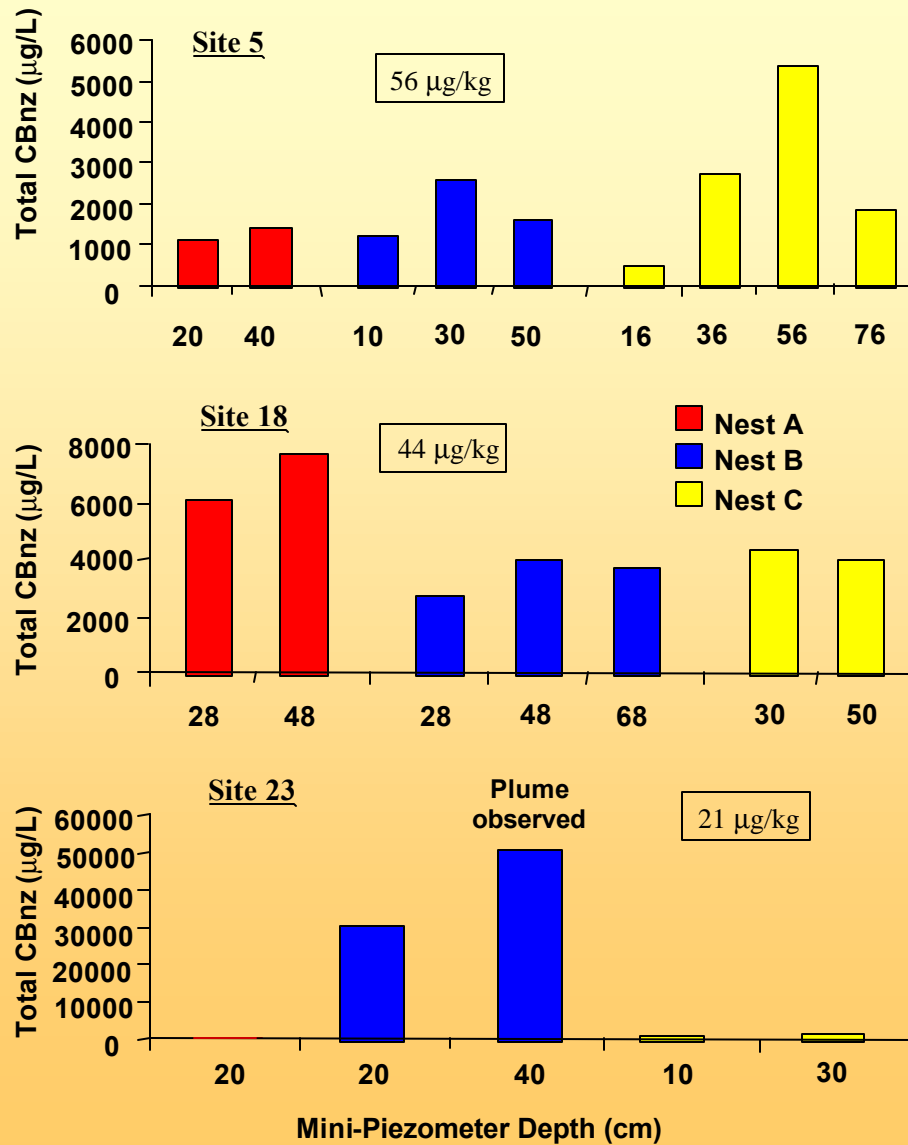
>100,000



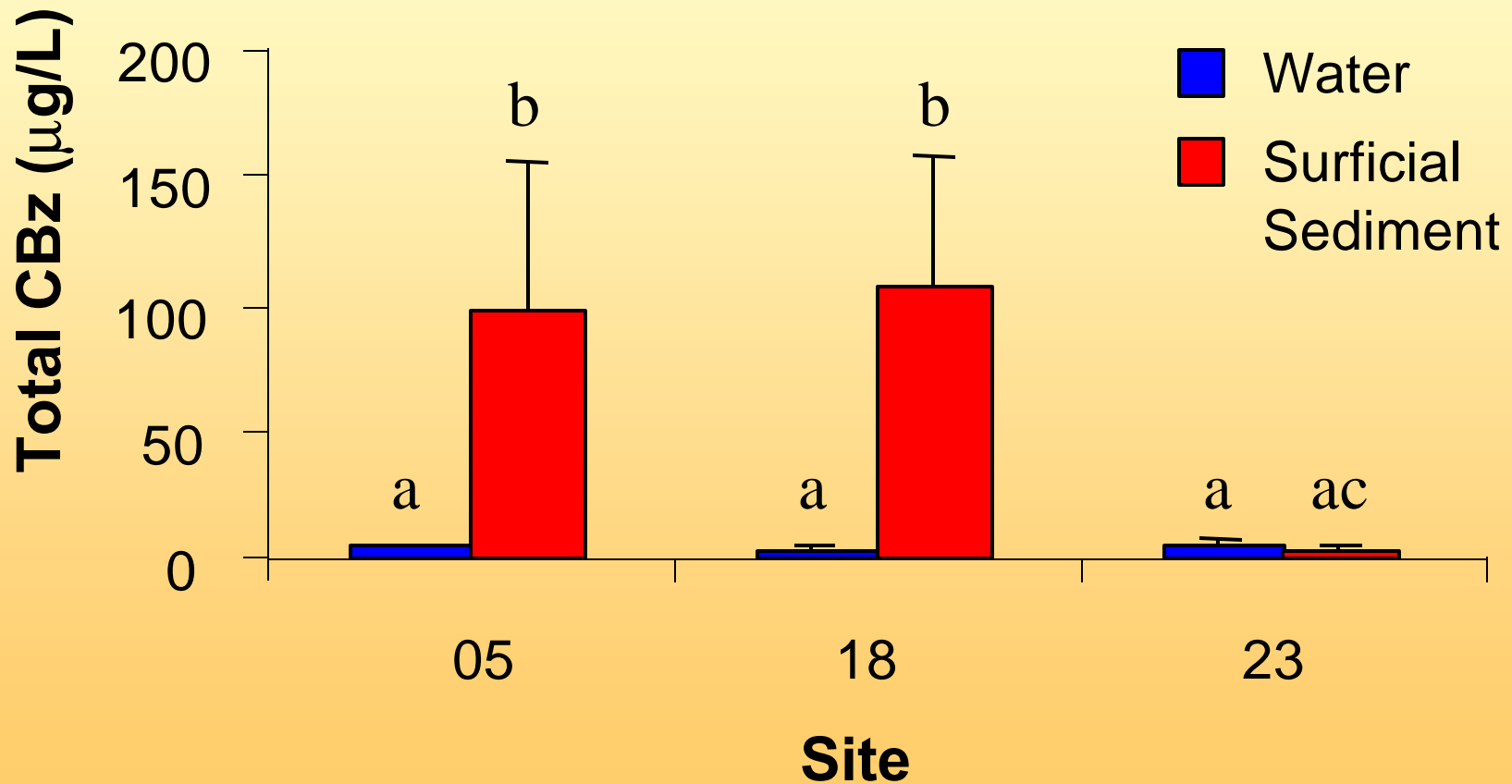
# Maine 1999: Hydraulic Heads



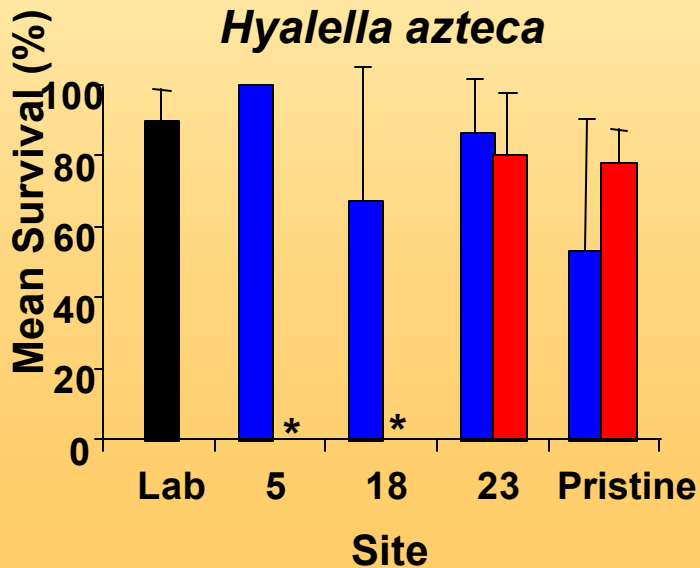
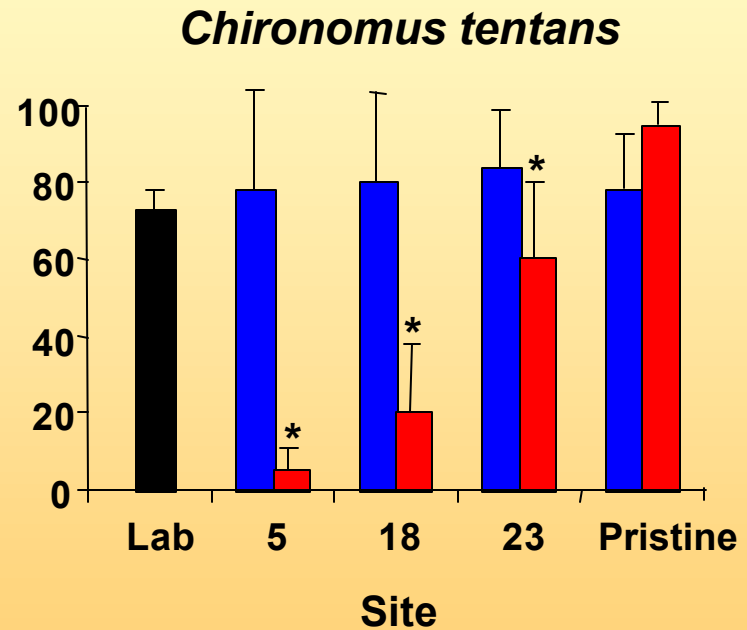
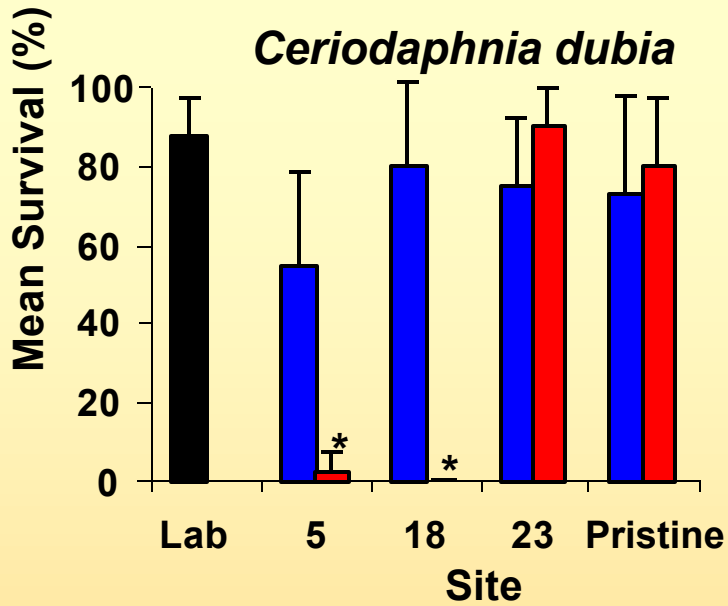
# Total Chlorobenzenes in Pore Water



# Total Chlorinated Benzene Exposure Levels Within *In Situ* Chambers



# In Situ Exposure Maine Chlorobenzene Study

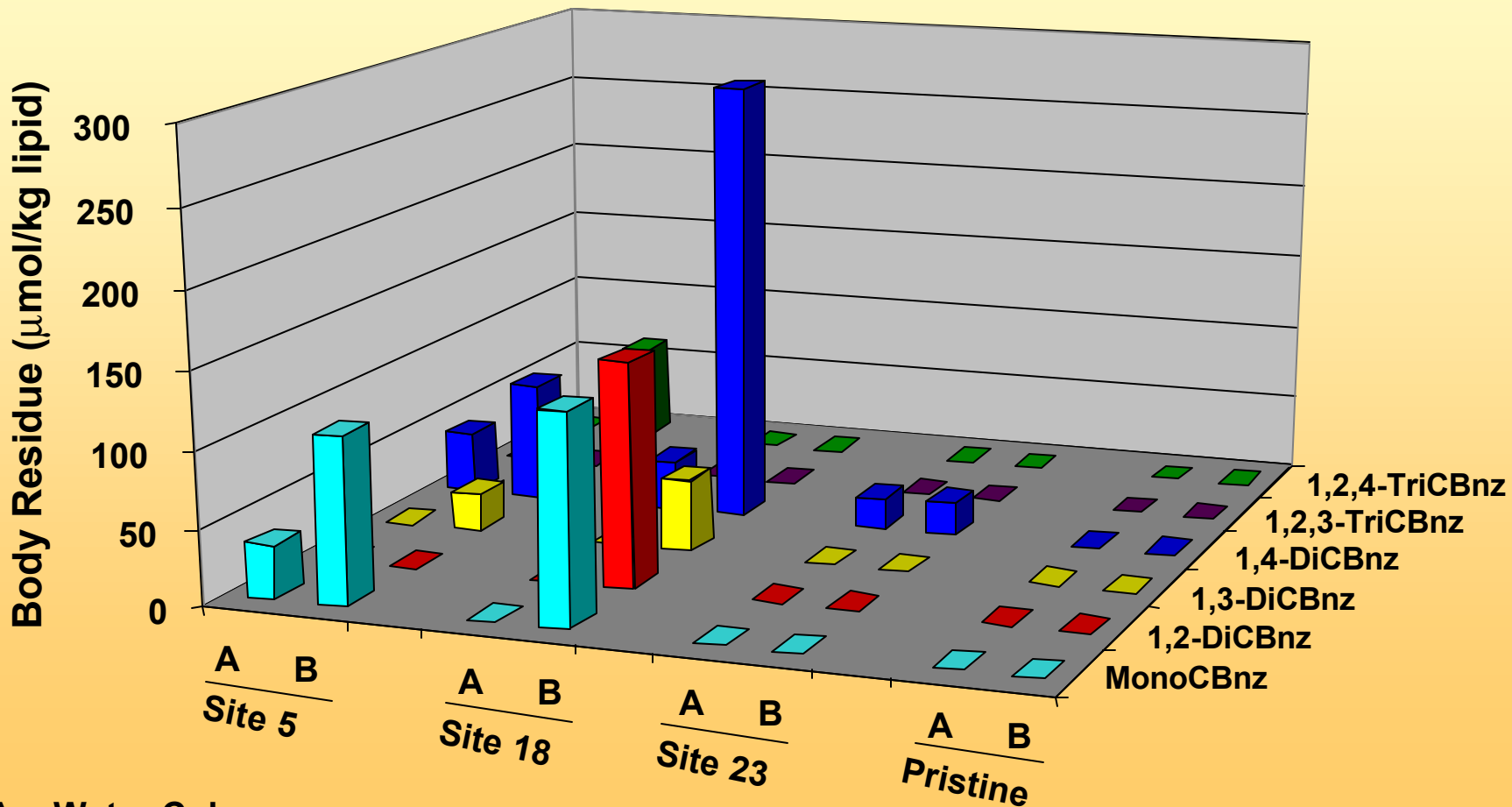


Water  
Surficial Sediment

\* Significantly different from field reference site, Pristine ( $p < 0.05$ )

(Greenberg, M.S. et al. *Environ. Toxicol. Chem.* 21(2):289-297, 2002)

# 96-h *In Situ* Bioaccumulation *L. variegatus*, Maine Chlorobenzene Study



A = Water Column  
B = Surficial Sediments

# Conclusions: Field Studies

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- Mini-piezometer data provide a unique *in situ* characterization approach--must document GW-SW conditions
- Data from mini-piezometers improved interpretation of exposure-effects relationships
- Downwelling was shown to reduce exposure in one system

# Conclusions: Field Studies

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- Upwelling conditions were shown to increase exposure and effects when sediments and groundwater were contaminated
- Integrated approaches are essential in a holistic assessment of sediment toxicity

# Bioaccumulation Model

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## Objectives

- Develop a bioaccumulation model that accurately predicts tissue concentrations for benthic species exposed to contaminated sediments
- Evaluate model by comparing predictions to *in situ* bioaccumulation at sites containing contaminated sediments



# Methods

## ➤ Laboratory:

- Model compounds: FLU and TF
- Toxicokinetics tests (sediment bioaccumulation; waterborne kinetics)
- Sediment desorption kinetics (Tenax<sup>®</sup>-TA beads)

## ➤ Model development:

- Parameterized with laboratory and literature data
- Used kinetic rate constants for pore water uptake
- Used desorption data to determine pore water concentrations
- Upwelling and downwelling included by addition of a pore water flow term

# Methods

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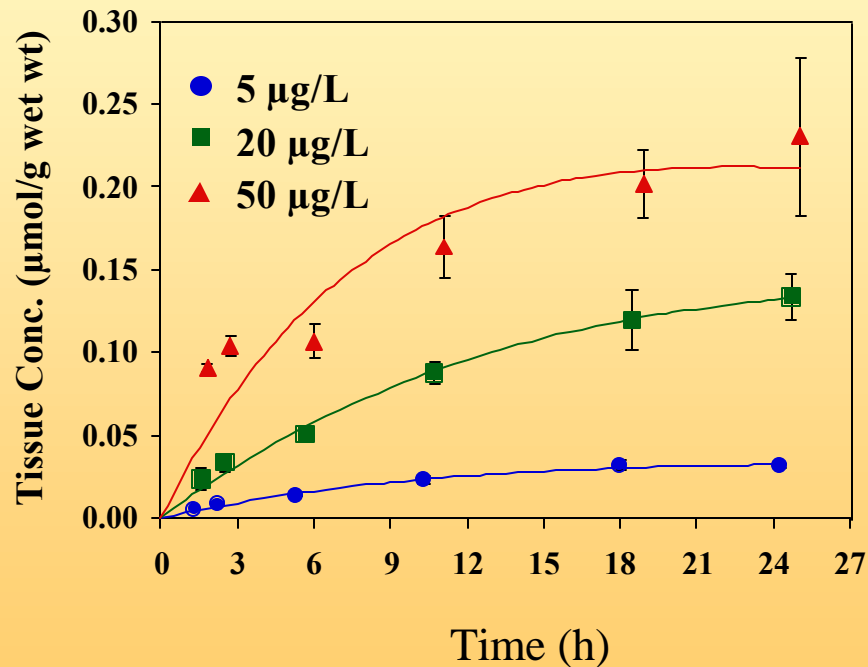
## ➤ Model validation:

- Bioaccumulation of chlorobenzenes by *in situ* exposed *L. variegatus* simulated
- Chlorobenzene parameters obtained from literature
- Simulated steady state concentrations compared to measured tissue residues

# Kinetics of waterborne FLU in *L. variegatus*

$$\frac{dC_a}{dt} = k_u C_w^0 e^{-\lambda t} - k_e C_a$$

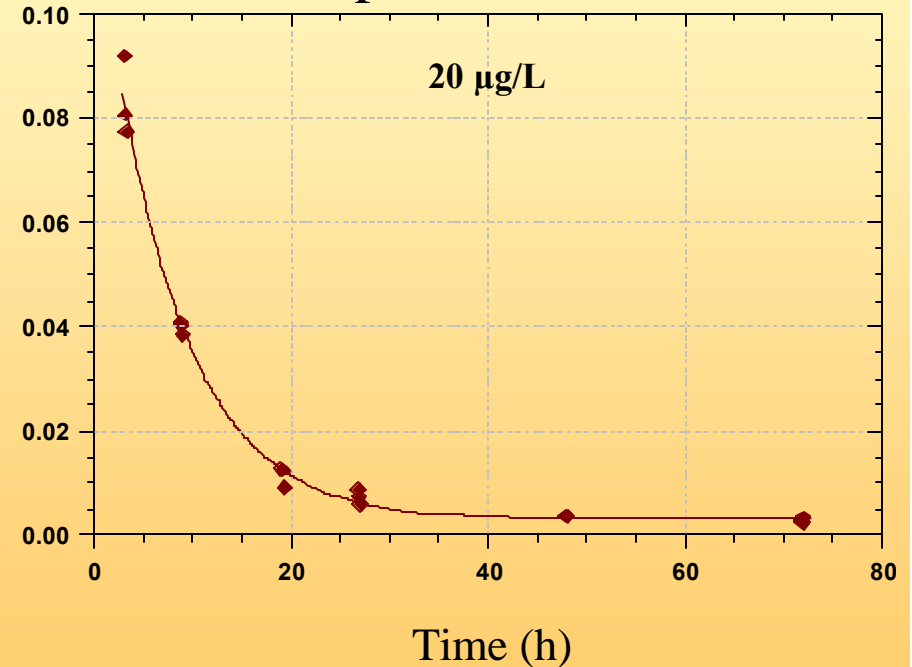
## Bioconcentration



$$k_u = 150 (\pm 14) \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$$

$$k_e = 0.076 (\pm 0.035) \text{ h}^{-1}$$

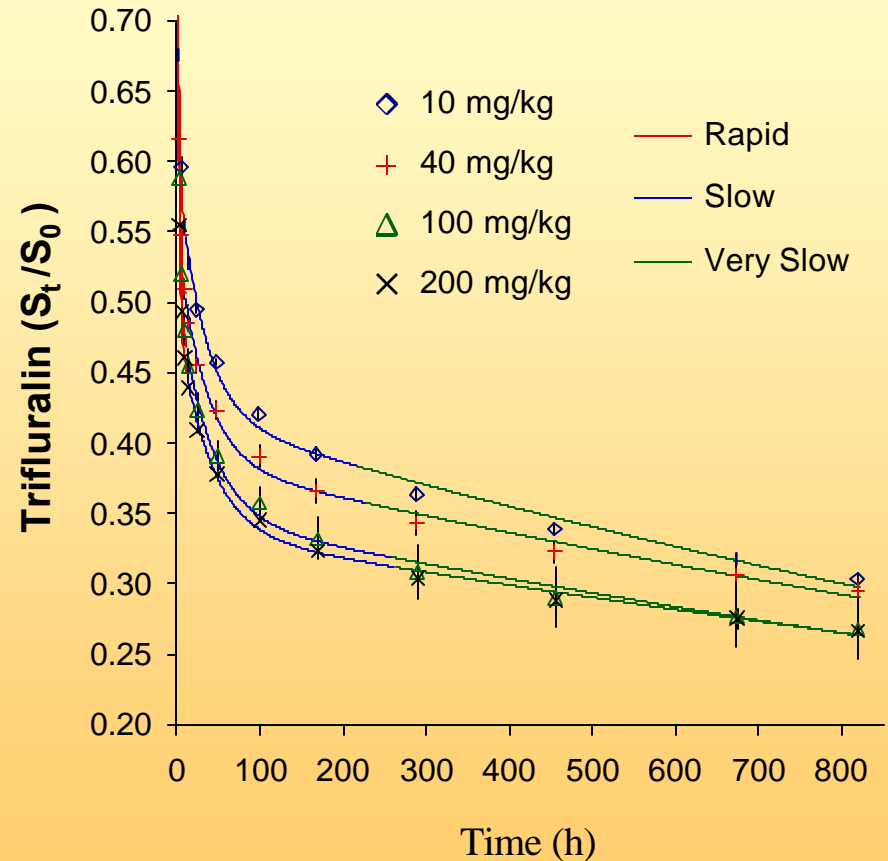
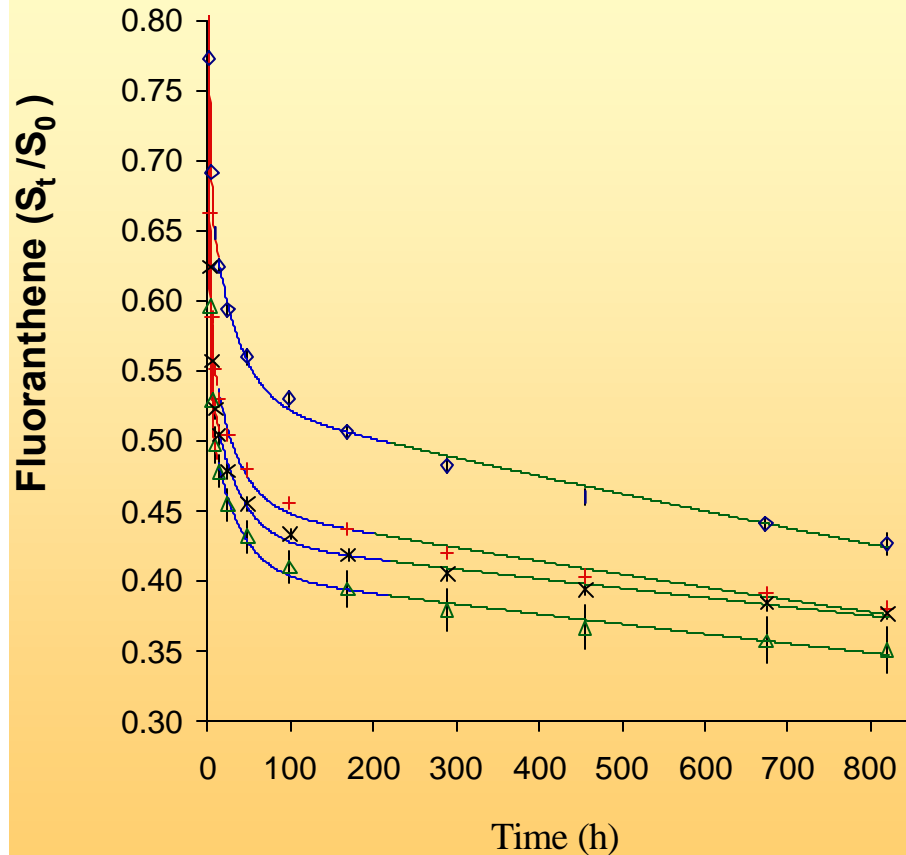
## Post-exposure elimination



$$k_{e(m)} = 0.13 (\pm 0.0035) \text{ h}^{-1}$$

# Desorption: Lake Huron Sediments

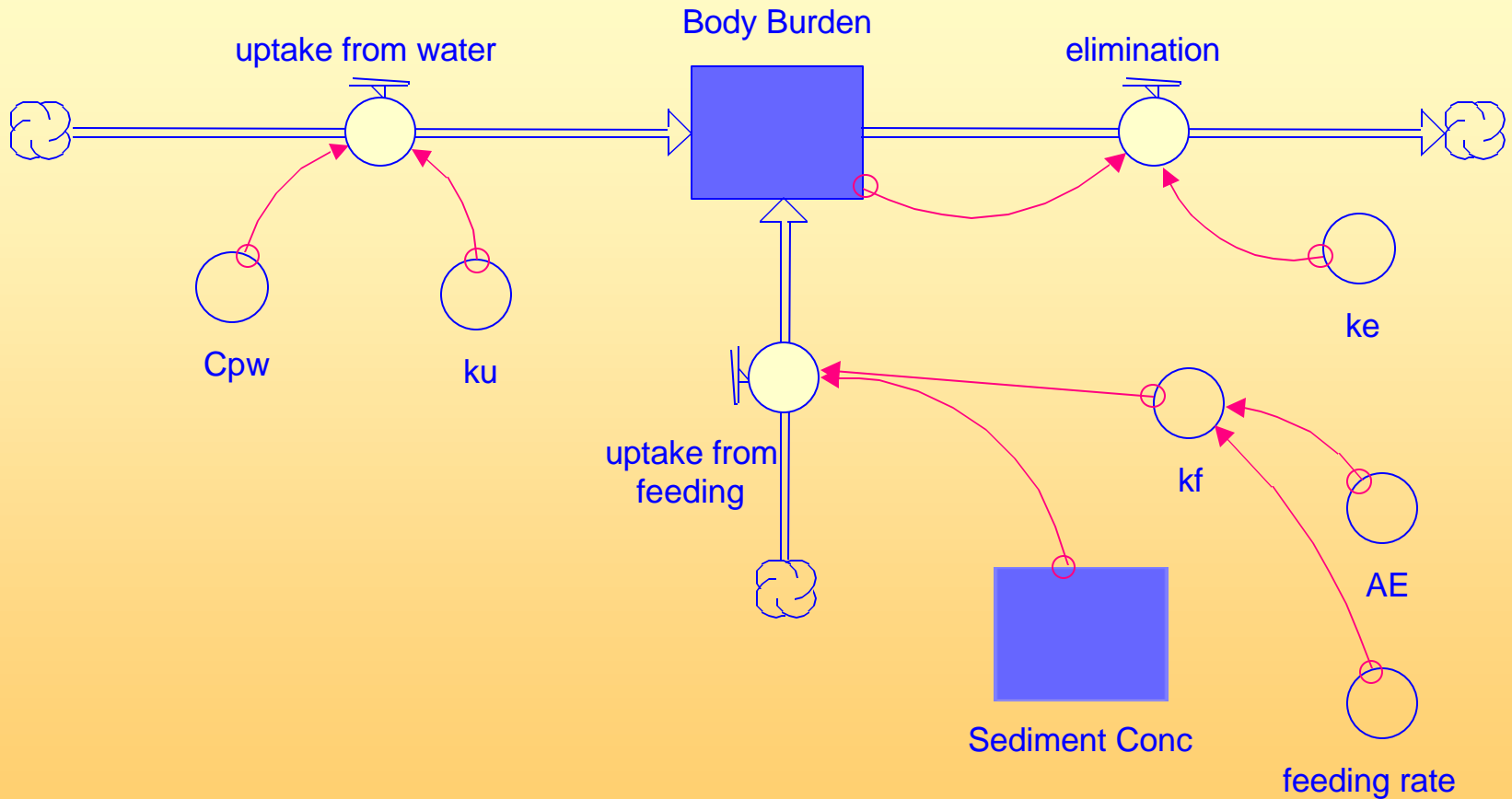
$$S_t / S_0 = F_{rapid} (e^{-k_{rapid} * t}) + F_{slow} (e^{-k_{slow} * t}) + F_{veryslow} (e^{-k_{veryslow} * t})$$



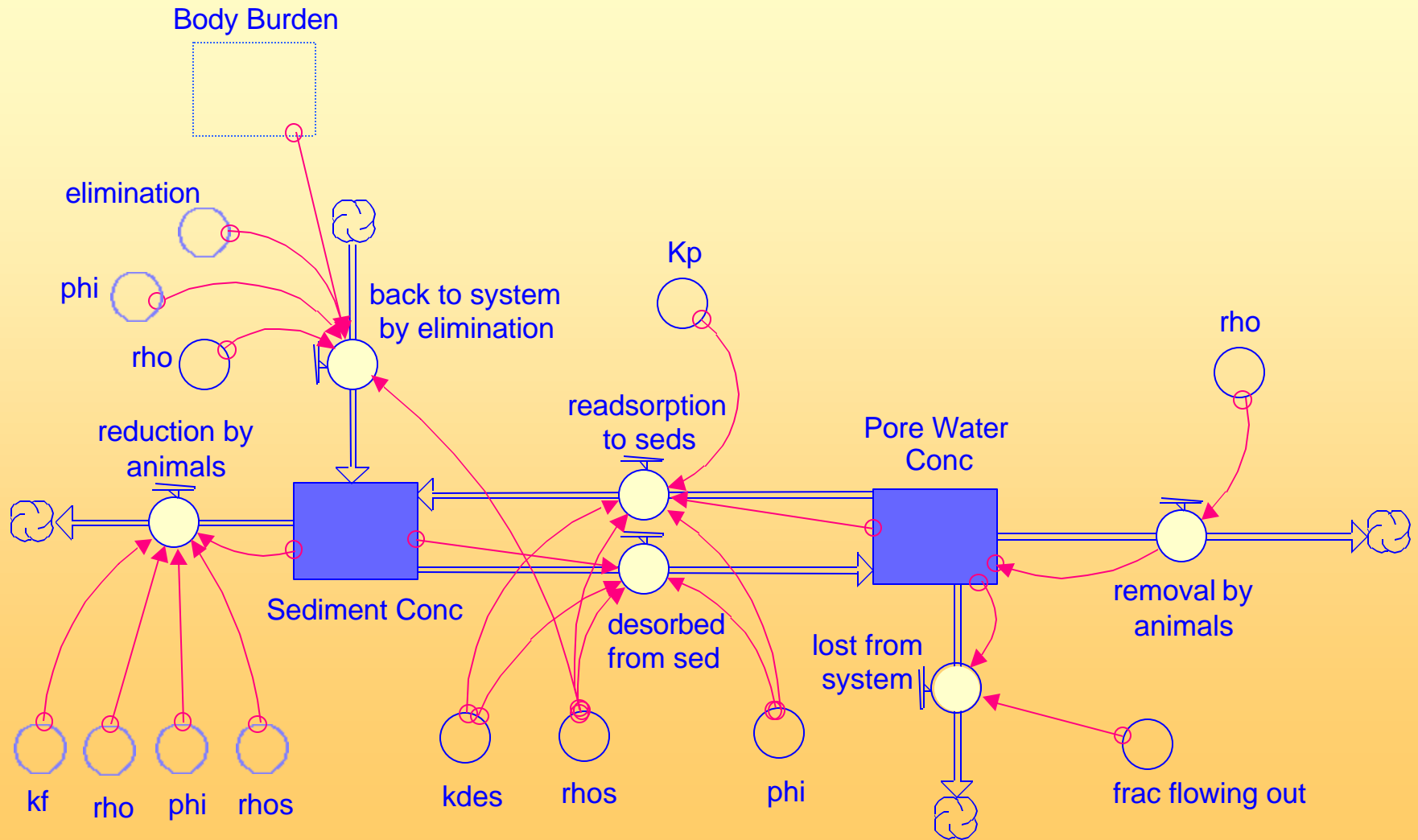
Desorption Rates:  
 $10^{-2} - 10^{-4} \text{ h}^{-1}$

Rapid  $t_{99.9}$  0.5 d  
 Slow  $t_{99.9}$  12 d  
 Very Slow  $t_{99.9}$  3 y

# Organism Sector

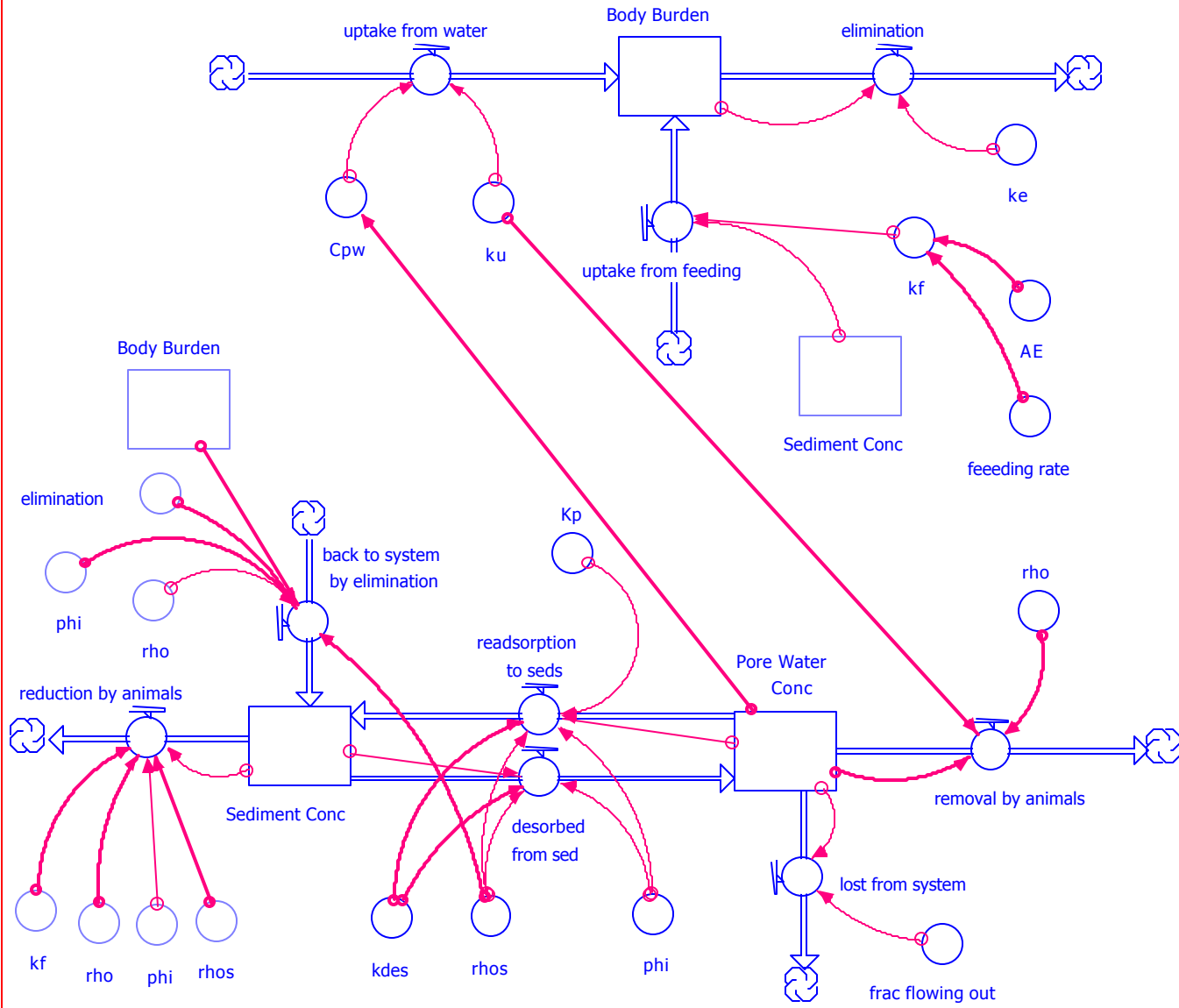


# Sediments & Pore Water Sector



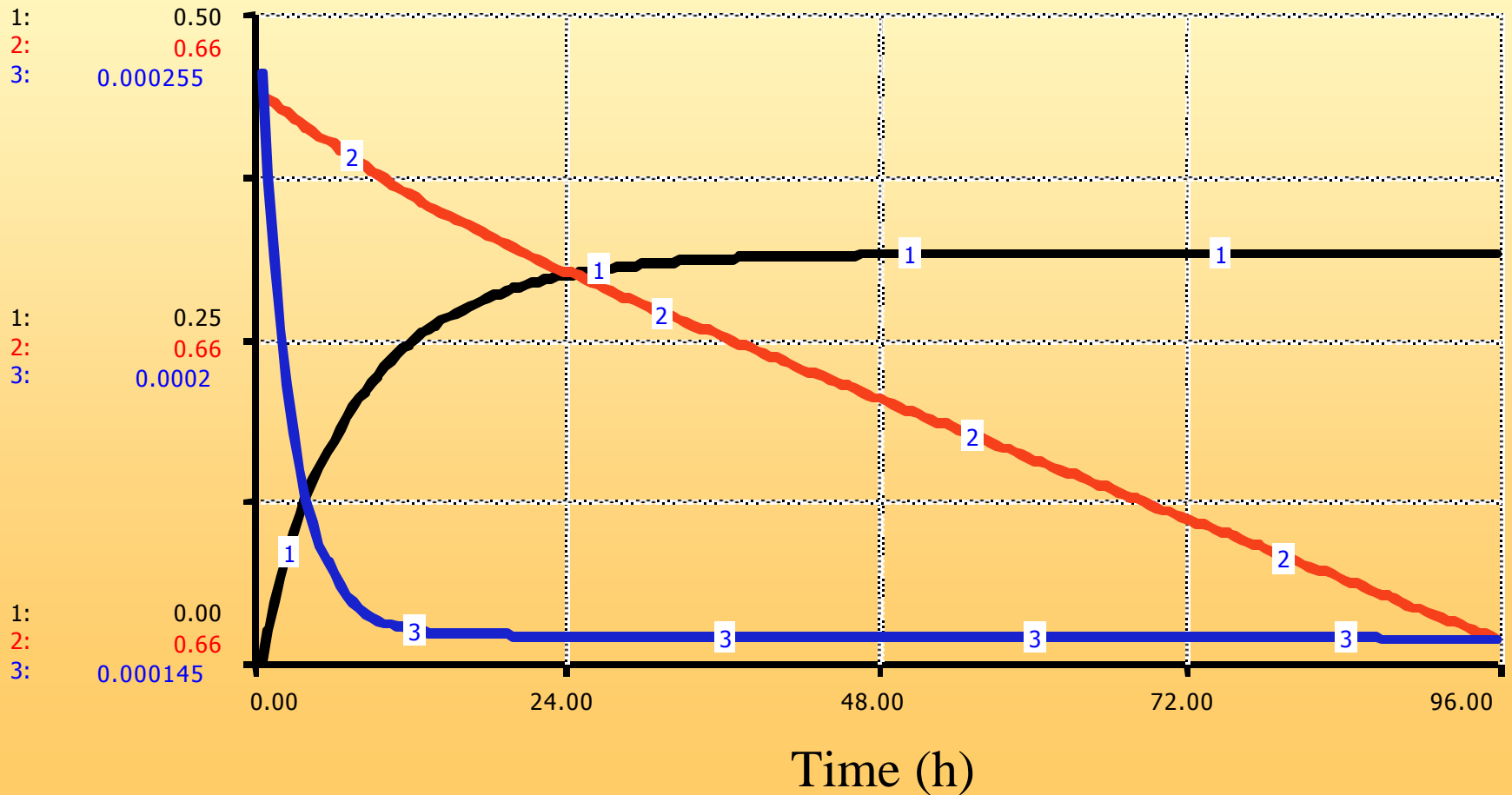


# Bioaccumulation Model



# Model output: No pore flow

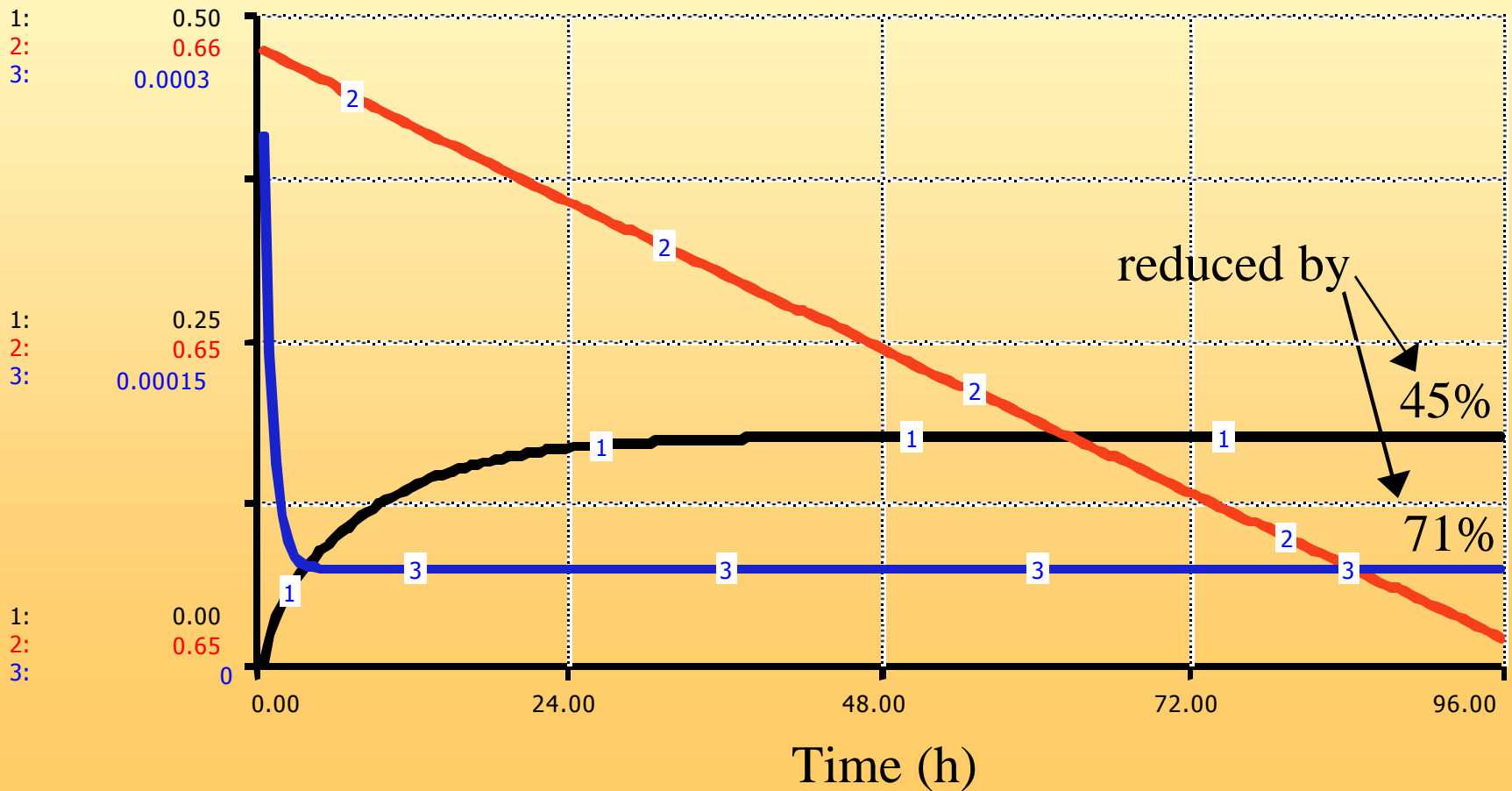
1. Body Burden ( $\mu\text{mol/g}$  wet wt)
2. Sediment Conc. ( $\mu\text{mol/g}$  dry wt)
3. Pore Water Conc. ( $\mu\text{mol/mL}$ )





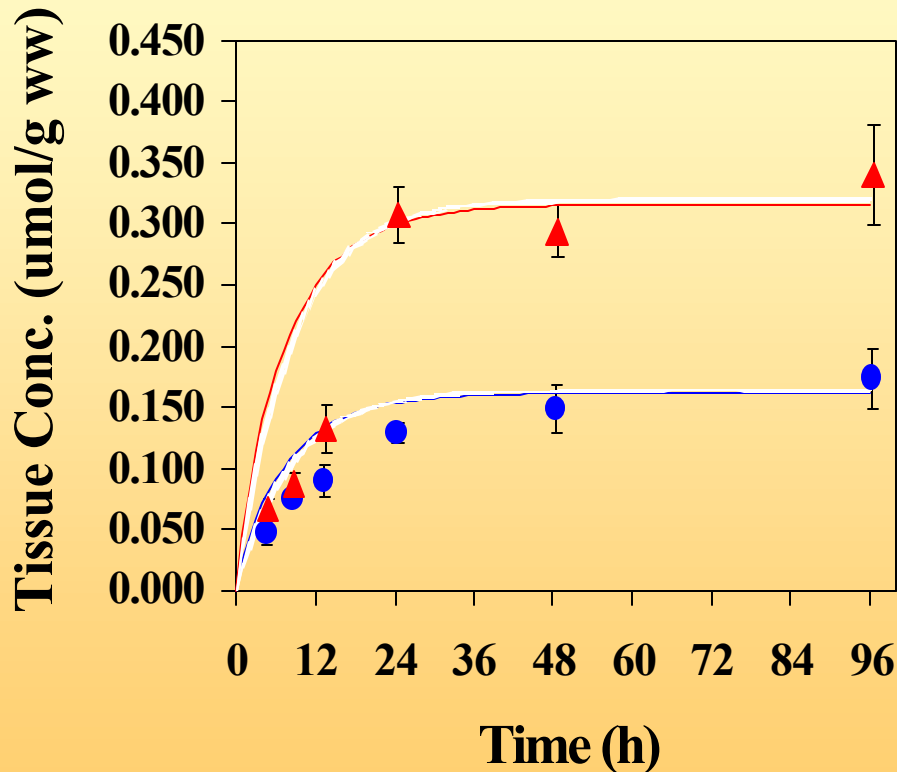
# Model output: Full pore flow

1. Body Burden ( $\mu\text{mol/g}$  wet wt)
2. Sediment Conc. ( $\mu\text{mol/g}$  dry wt)
3. Pore Water Conc. ( $\mu\text{mol/mL}$ )

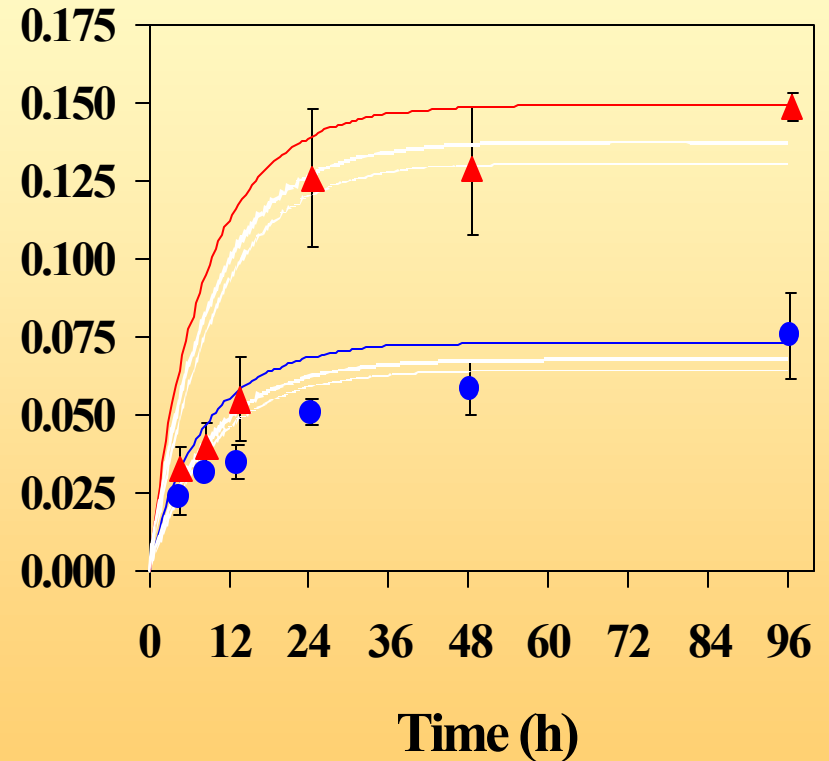


# Model predictions and experimental tissue concentrations: Lake Erie, *L. variegatus*

## A) Fluoranthene



## B) Trifluralin



### Legend

- |                  |             |             |
|------------------|-------------|-------------|
| ● 100 mg/kg dose | — 100 Sim 1 | — 200 Sim 1 |
| ▲ 200 mg/kg dose | — 100 Sim 2 | — 200 Sim 2 |
|                  | — 100 Sim 3 | — 200 Sim 3 |

# Field validation for 1,4-dichlorobenzene

| Compound | Site | Measured body burden (μmol/g wet wt) | Predicted body burden (μmol/g wet wt) | Factor | Parameter and value   |
|----------|------|--------------------------------------|---------------------------------------|--------|---|
| 1,4-DiCB | 5    | 1.02e-03                             | 1.12e-03                              | 1.09   | k <sub>u</sub> = 0.070<br>k <sub>e</sub> = 0.257<br>FR = 0.01<br>q = 0.10 |
|          | 18   | 3.74e-03                             | 5.64e-03                              | 1.51   | k <sub>u</sub> = 0.070<br>k <sub>e</sub> = 0.257<br>FR = 0.01<br>q = 0.10 |
|          | 23   | 2.31e-04                             | 1.49e-03                              | 6.43   | k <sub>u</sub> = 0.070<br>k <sub>e</sub> = 0.257<br>FR = 0.01<br>q = 1.00 |
|          |      |                                      | 2.35e-04                              | 1.02   | k <sub>u</sub> = 0.070<br>k <sub>e</sub> = 0.257<br>FR = 0.00<br>q = 0.25 |

# Conclusions

- The model adequately reproduced the  $C_{ss}$  observed in laboratory sediment exposures
- Predictions of field bioaccumulation data that were 4 provided a degree of validation of the model
- Qualitative description of upwelling and downwelling in the model indicated that this term is an important determining factor in bioavailability
- The model simulations suggested that *in situ* rates of feeding should be measured, as FR is a sensitive parameter.

# The Future...

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- Future research will be designed to improve characterization of GSI to improve the modeling of the impact of upwelling and downwelling on exposure, effects and bioaccumulation.