INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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FIRST AUTUMN WORKSHOP ON MATHEMATICAL ECOLOGY

(31 October - 18 November 1988)

PHYSICAL-CHEMICAL-BIOLOGICAL MODELLING OF THE FATE OF TOXIC SUBSTANCES IN AQUATIC SYSTEMS

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Mathematical Ecology Workshop
Nov. 1988

Physical-Chemical-Biological Modeling of the Fate of Toxic Substances in Aquatic Systems

Outline of Lectures

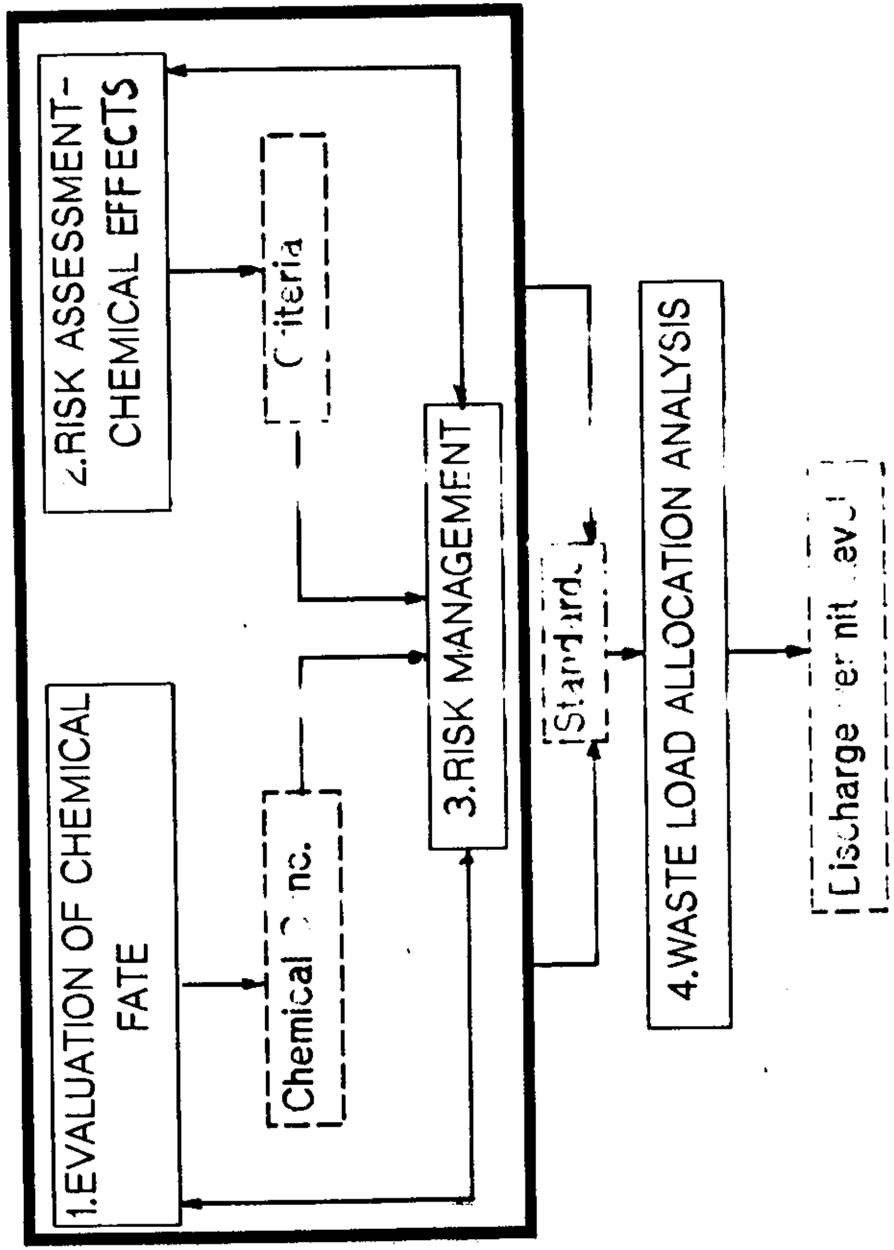
Robert V. Thomann
Manhattan College

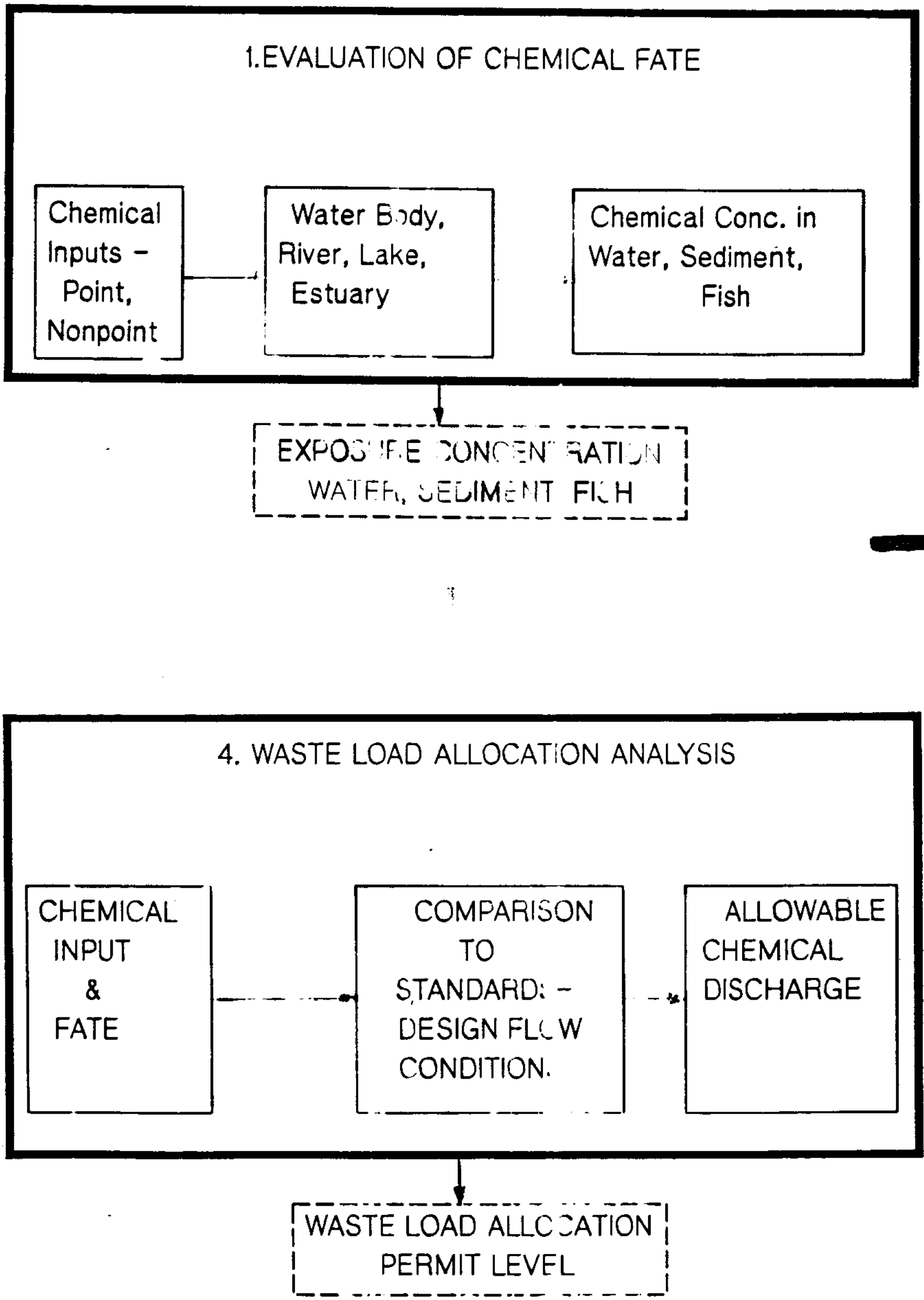
#1 - INTRODUCTION
CHEMICAL FORMS

#2 - Physical-Chemical Modeling

#3 - Bioconcentration & Bioaccumulation

Applications - Rivers
Great Lakes
Hudson Estuary




1.EVALUATION OF CHEMICAL FATE
Chemical Inputs – Point, Nonpoint
Water Body, River, Lake, Estuary
Chemical Conc. in Water, Sediment, Fish
EXPOSURE CONCENTRATION WATER, SEDIMENT FISH
4. WASTE LOAD ALLOCATION ANALYSIS
CHEMICAL INPUT & FATE
COMPARISON TO STANDARDS – DESIGN FLOW CONDITION.
ALLOWABLE CHEMICAL DISCHARGE
WASTE LOAD ALLOCATION PERMIT LEVEL

PAHO8607

Components of a

Toxic Substances Program
for Surface Waters

I - Identification of Problems -
Potential or Actual

A. Determine Sources
- Industrial Complexes
- Mining
- Pesticide Use
- Cities

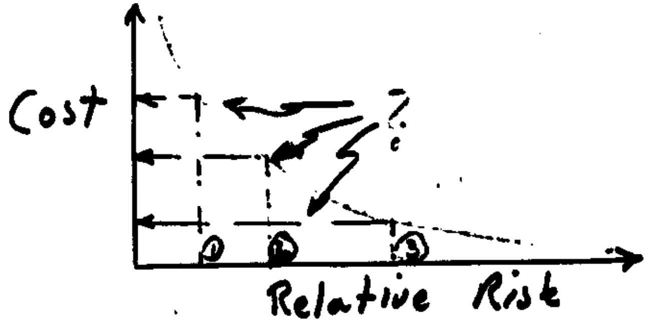
B. Determine Affected Water Uses
- Public Health
- Ecology

II. Establish Water Quality / Fish Standards + Evaluate Risk

III. Evaluate Fate + Effect of Toxic Substance
- A. Mathematical Model of fate ⇒ concentration.
- B. Concentration ⇒ Effect

IV. Evaluate Alternatives to Meet Standards + Various Risk Levels

V. Determine "cost effective" Alternative - Cost / Benefit Risk Analysis



VI. Establish allowable release of chemical to water body

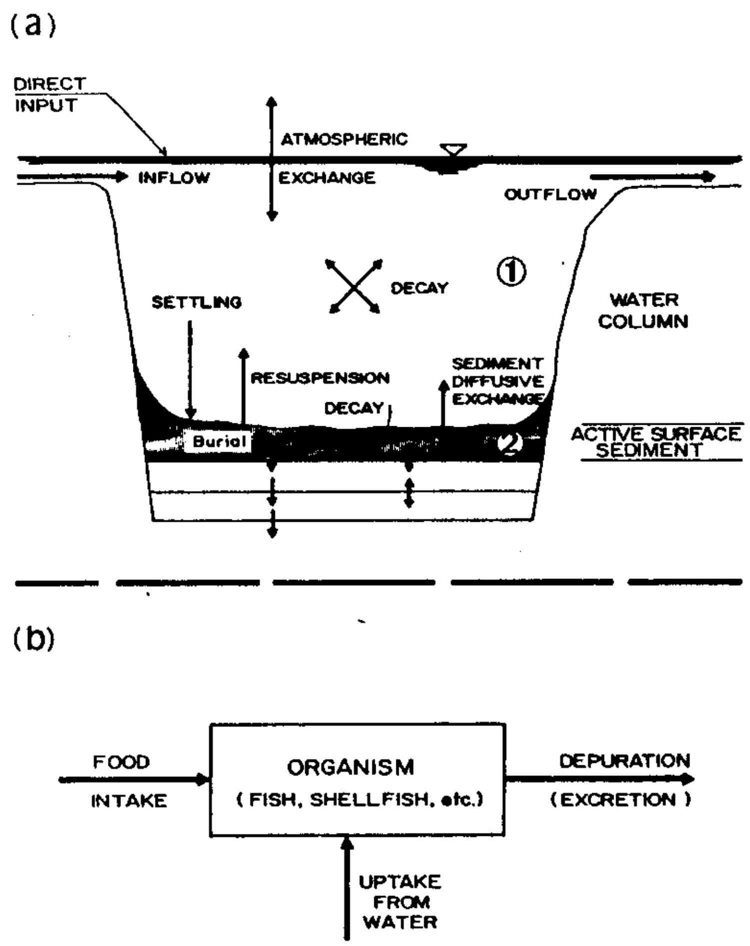
VII. Monitor discharges, water, eco-system

TABLE 3-2

Some Guidelines for Drinking-Water Quality as Recommended by The World Health Organization (1984a,b)

Constituents of Health Significance

Constituent	Guideline Value (µg/ℓ unless noted)	Remarks
Arsenic	50	
Cadmium	5	
Chromium	50	
Cyanide	100	
Fluoride	1500	Natural or deliberately added; local or climatic conditions may necessitate adaptation
Lead	50	
Mercury	1	
Nitrate	10(mgN/ℓ)	
Selenium	10	
Aldrin & dieldrin	30	
Benzene	10[a]	
Benzo[a]pyrene	0.01[a]	
Carbon tetrachloride	3[a]	Tentative guideline value[b]
Chlordane	0.3	
Chlorobenzenes	No guideline set	Odor threshold between 0.1 and 0.3 µg/ℓ.
Chloroform	30[a]	Disinfection efficiency must not be compromised when controlling chloroform content.
Chlorophenols	No guideline set	Odor threshold concentration, 0.1 µg/ℓ.
2,4-D	100[c]	
DDT	1	
1,2-dichlorethane	10[a]	
1,1-dichloroethene[d]	0.3[a]	



Primary Forms of Toxicant

a. c_d' - dissolved concentration
Mass of chemical / vol. of water
$[M_T / L_w^3 ; \mu g/l]$

b. r - particulate concentration
chemical sorbed to solids
Mass of chemical / Mass of solids
$[M_T / M_s ; \mu g/g(\text{dry solids})]$

c. c_g - gaseous phase concentration
Mass of chemical / vol. of air
$[M_T / L_g^3 ; \mu g/l]$

d. ν - concentration in organism
Mass of toxicant / Mass of organism
$[M_T / M_o ; \mu g/g(\text{wet weight})]$

Relationships Between Forms

c_p = particulate form, bulk volume basis
$[M_T / L_{s+w}^3 ; \mu g/l(\text{bulk})]$

$= r\,m$; m = solids conc. $[M_s / L_{s+w}^3]$

$\frac{\mu g}{l} = \frac{\mu g}{g} \frac{g}{l}$

c_T = total chemical conc. $[M_T / L_{s+w}^3]$

$= c_p + c_d'$ ← $\mu g/l_{water}$
$\mu g/l(\text{bulk})$

or more correctly,

$c_T = c_p + \phi\, c_d'$
↑
where ϕ = porosity of sediment
$[L_w^3 / L_{s+w}^3]$

$\therefore\ c_T = c_p + c_d$ (porosity corrected)

Note: $m = \rho_s (1 - \phi) \cdot 10^6$

$\frac{mg}{l}$ $\frac{g}{cm^3}$

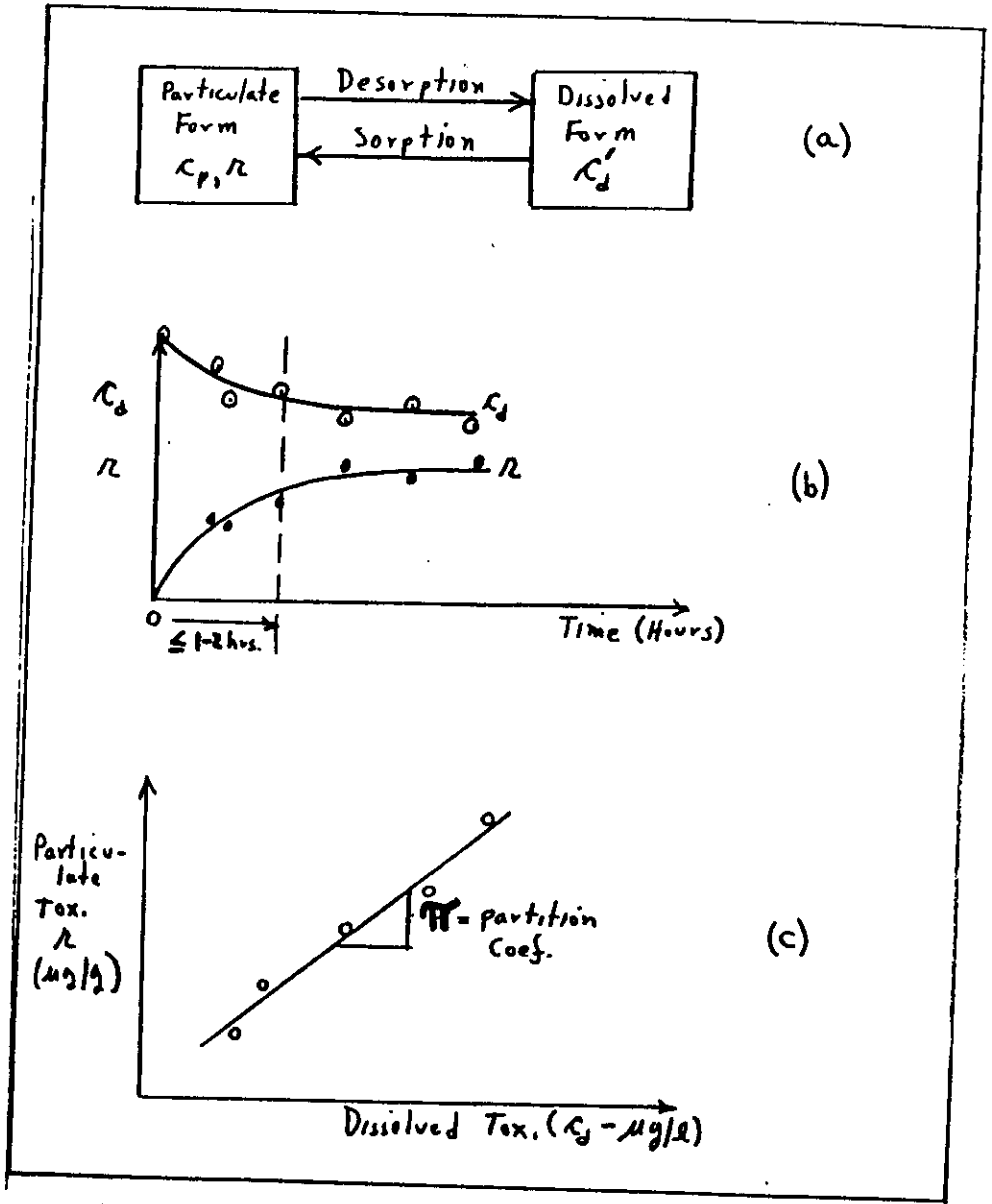
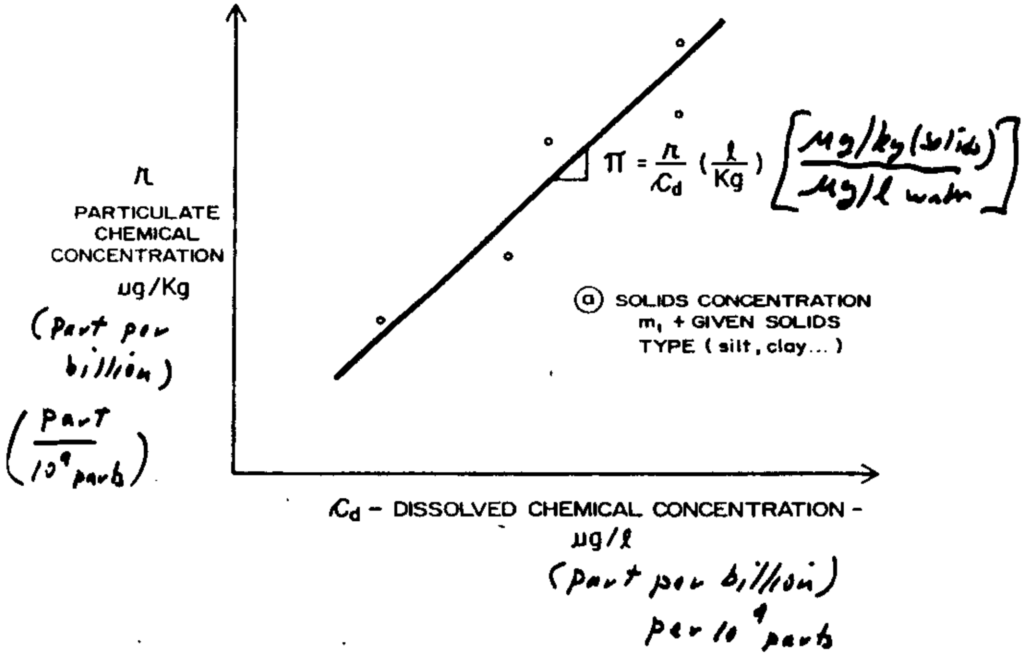


Fig. 9-5 a) Sorption-Desorption of Toxicant, b) "Fast" Kinetic Relationships of Sorption, c) Partition Coefficient as Slope of Particulate vs. Dissolved Chemical



Fraction of chemical in Dissolved & Particulate Forms

From partition coef:

$$r = c_d \Pi$$

$(\mu g/kg) \quad (\mu g/L)(L/kg)$

Also:

$$c_T = c_p + c_d = rm + c_d$$

$$\therefore \quad c_T = (1 + \Pi m) c_d$$

and

$$c_d = \left(\frac{1}{1+\Pi m}\right) c_T = f_d c_T$$

where f_d = fraction of total chemical in dissolved form

Particulate Form:

$$c_p = \left(\frac{\Pi m}{1+\Pi m}\right) c_T = f_p c_T$$

where f_p = fraction of total chemical in particulate form

$$f_d + f_p = 1$$

Simple Example

Two chemicals: PCB - $\Pi = 10^5$ L/kg

Napthalene - $\Pi = 10^3$ L/kg

Solids concentration = 100 mg/L

For PCB:

$$f_d = \frac{1}{1 + 10^5\left(\frac{L}{kg}\right) 100\left(\frac{mg}{L}\right) \frac{kg}{10^6\, mg}} = 0.09$$

$$f_p = 1 - .09 = 0.91$$

For Napthalene:

$$f_d = \frac{1}{1 + 10^3(100)/10^6} = 0.91$$

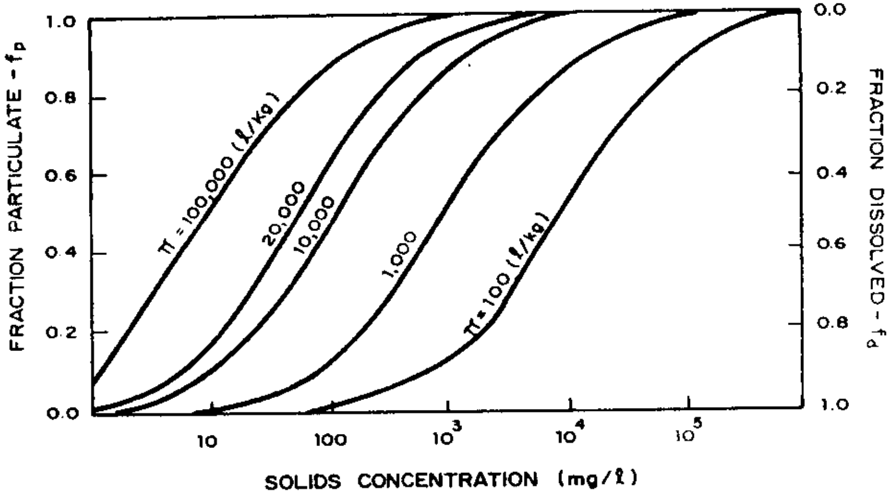
$$f_p = 0.09$$

m = 100 mg/L

Π	Chemical	% Dissolved	% Particulate
10^3 L/kg	Napthalene	91	09
10^5 L/kg	PCB	09	91

$$\Pi_{sed} \approx \frac{f_{oc}}{DOC}$$

$$\frac{f_{oc} K_{ow}}{1 + DOC\, K_{ow}}$$



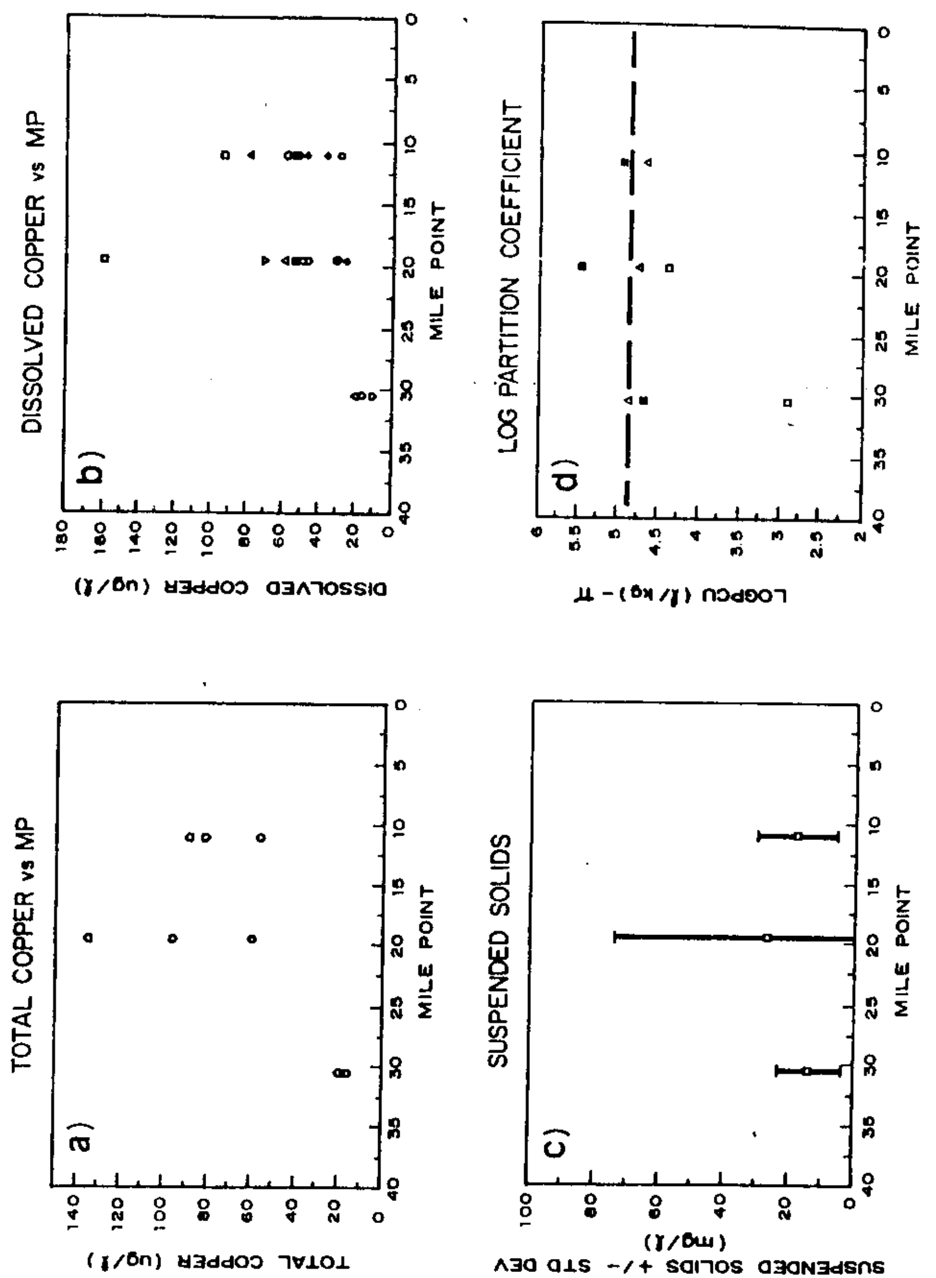
Under equilibrium "fast kinetics"

Fraction of chemical in dissolved form; f_d:

$$f_d = (1+\pi m)^{-1}$$

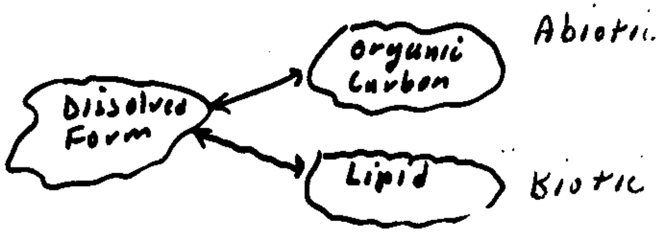
Fraction of chemical in particulate form, f_p:

$$f_p = \pi m(1+\pi m)^{-1}$$



Empirical Relationships for Π

Basic Idea: Hydrophobic chemicals partition primarily



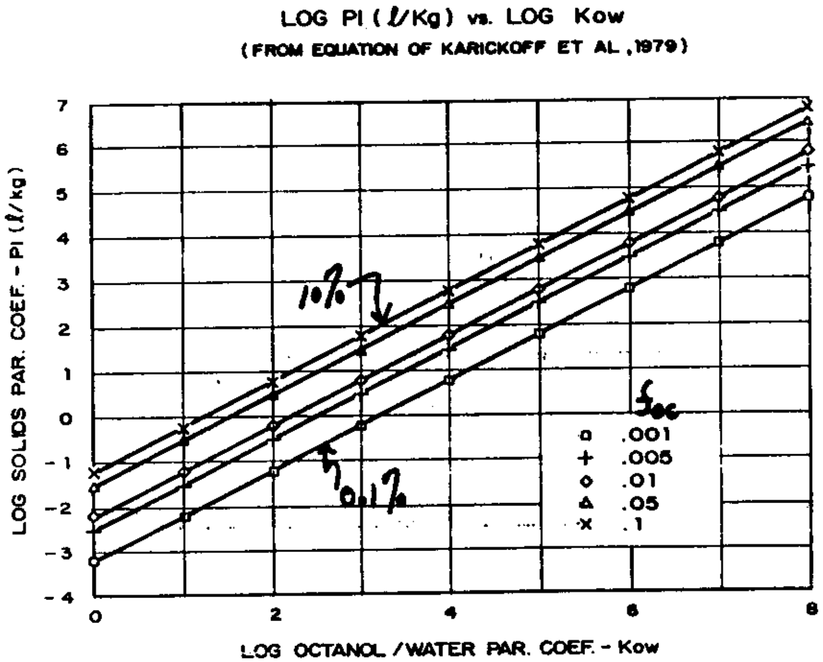
One measure: octanol/water partition coef = property of chemical

$$K_{ow} = \frac{\mu g/L\,(\text{octanol})}{\mu g/L\,(\text{water})}$$

Empirically have found

$$K_{oc} \approx K_{ow}$$

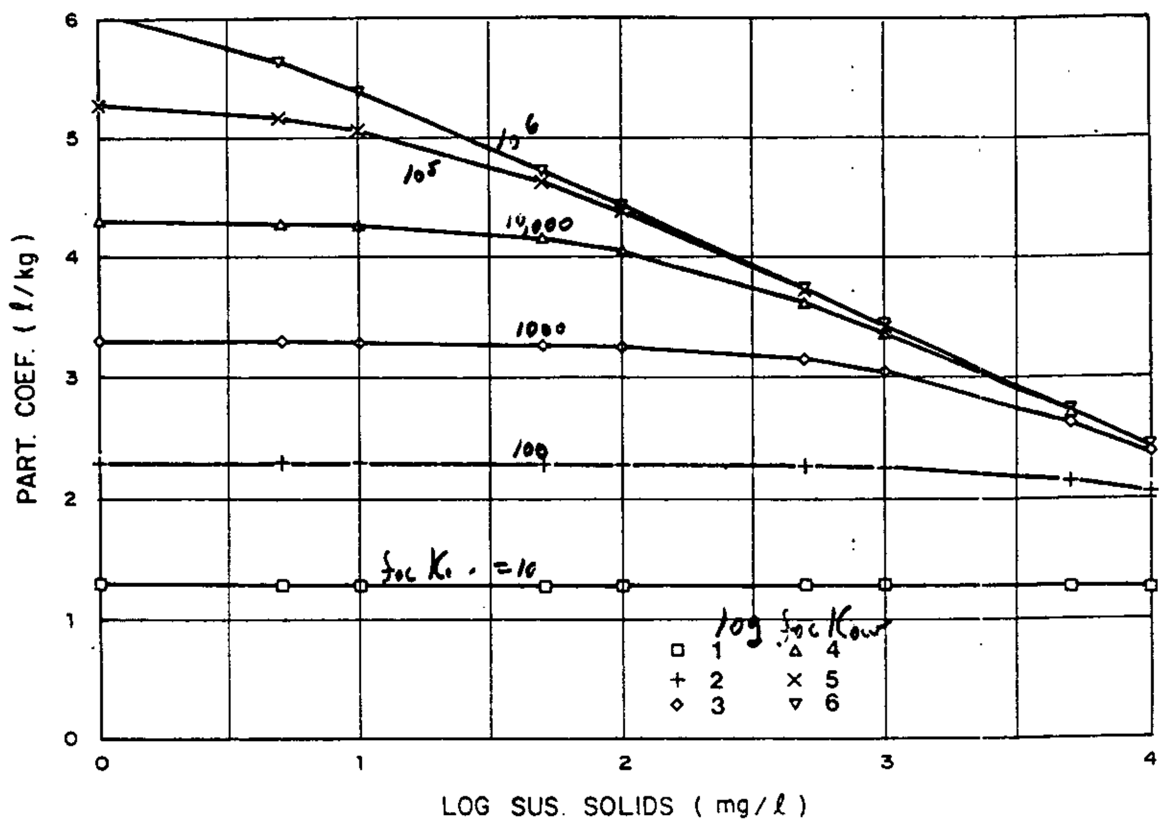
$$\frac{(\mu g/kg(C) \;/\; \mu g/L(\text{water}))}{\dfrac{L}{kg(\text{org carb})}}$$



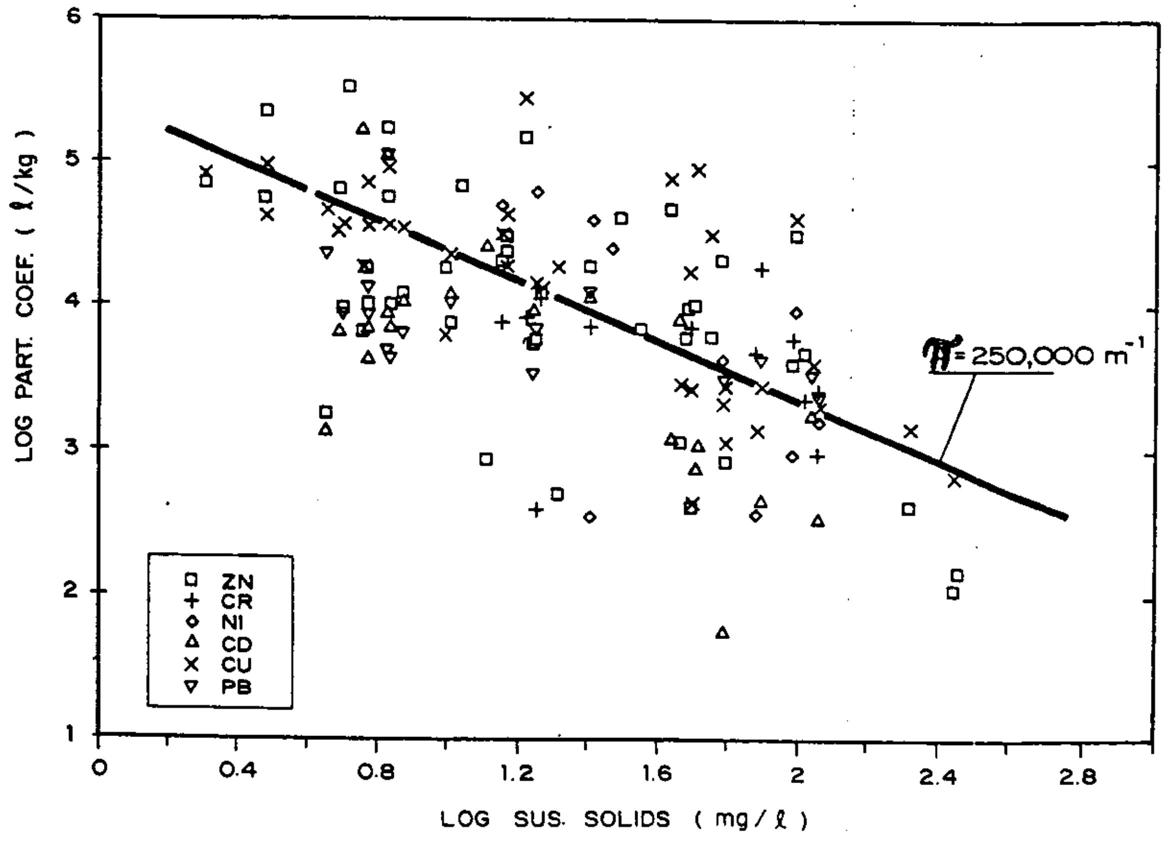
$$\Pi = 0.617\, f_{oc} K_{ow} \left(= 0.617\, f_{oc} K_{oc}\right)$$

where f_{oc} = fraction organic carbon $[M_{oc}/M_s]$

PARTITION COEF. (ℓ/kg) (DI TORO, 1985)
PI vs. SS for LOG (foc Kow)



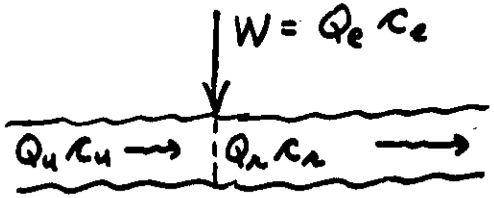
PARTITION COEF. vs SOLIDS
ALL RIVERS, ALL METALS



Waste Load Allocation and Water Quality Criteria

Issues:
1) Acute & chronic effects
2) Exposure time
   a) Averaging period
3) Return period of "design flow"

Mass Balance @ outfall:



$$c_r = \frac{Q_u c_u + Q_e c_e}{Q_u + Q_e}$$

Assume upstream conc = 0
$\therefore c_u = 0$

For a "target" concentration in the river after mixing $= c_r$, the allowable waste load is

$$W_{allow} = c_r \, (Q_u + Q_e)$$

$$[M/T] = \left[\frac{M}{L^3}\right]\left[\frac{L^3}{T}\right]$$

In terms of allowable effluent concentration, $(c_e)_{allow}$:

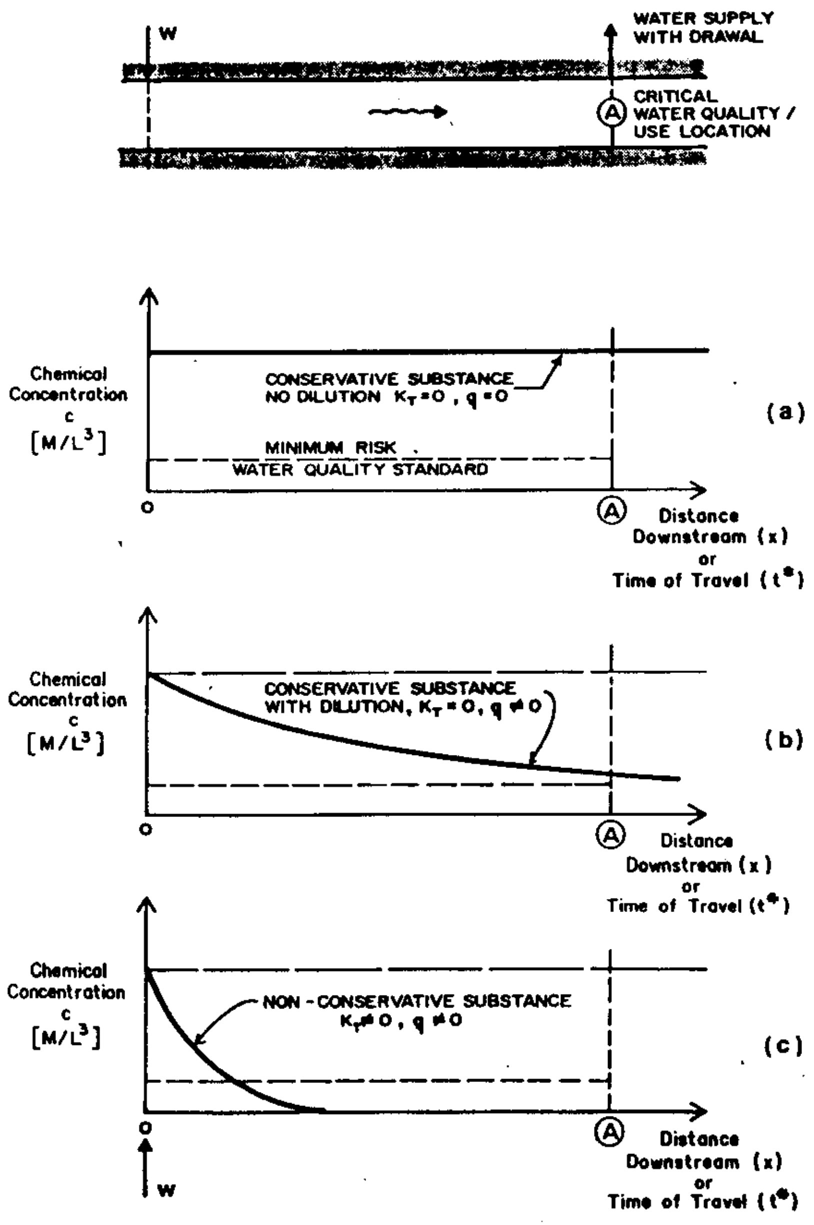
$$(c_e)_{allow} = c_r \left[\frac{Q_u + Q_e}{Q_e}\right]$$

or let R = dilution ratio $= Q_u / Q_e$ (0→∞)

$$(c_e)_{allow} = c_r \, (1 + R)$$

Limits: [illegible] for $R = 0$ ($Q_u = 0$)
for $R \to \infty$ ($Q_e = 0$)

Fig. 3-7: ILLUSTRATION OF POSSIBLE DOWNSTREAM FATE OF CHEMICALS OR TOXICITY



Downstream Fate of Chemical

Basic Eq.:

$$c = c_0 \exp\left[-(K_T + q)\,t^*\right]$$

c = conc. of chemical $[M/L^3]$ after mixing

c_0 = " " " at outfall

K_T = net chemical loss rate $[1/T]$

q = flow dilution rate $[1/T]$

t^* = time of travel $= \frac{x}{u} = \frac{\text{dist.}}{\text{vel.}}$

Net chemical Loss Rate:

$$K_T = \left(K_d + \frac{k_e}{H}\right) f_d + \frac{v_n}{H} f_p$$

K_d = decay rate $[1/T]$

k_e = volatilization rate $[1/T]$

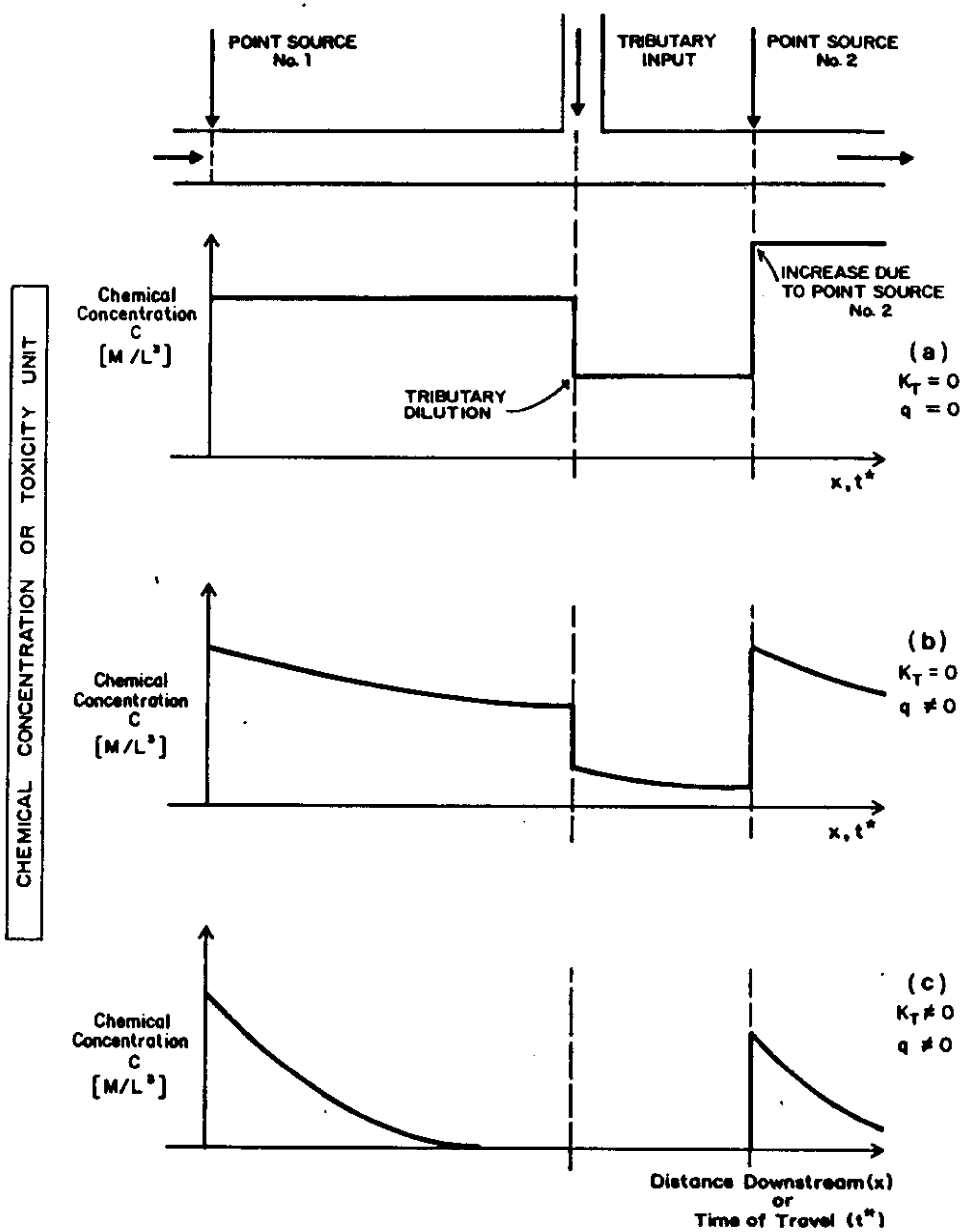
v_n = net loss of solids $[L/T]$

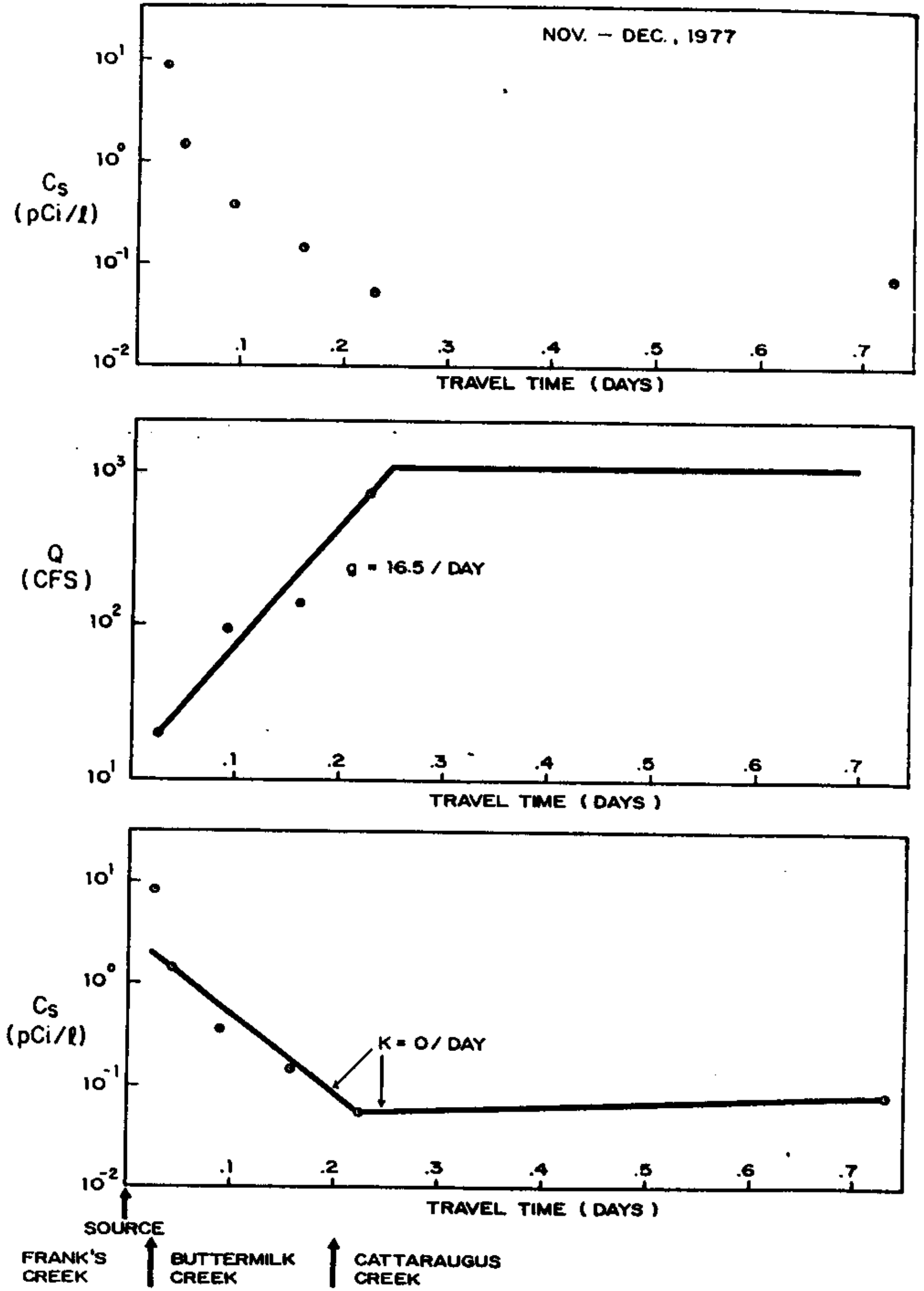
H = stream depth $[L]$

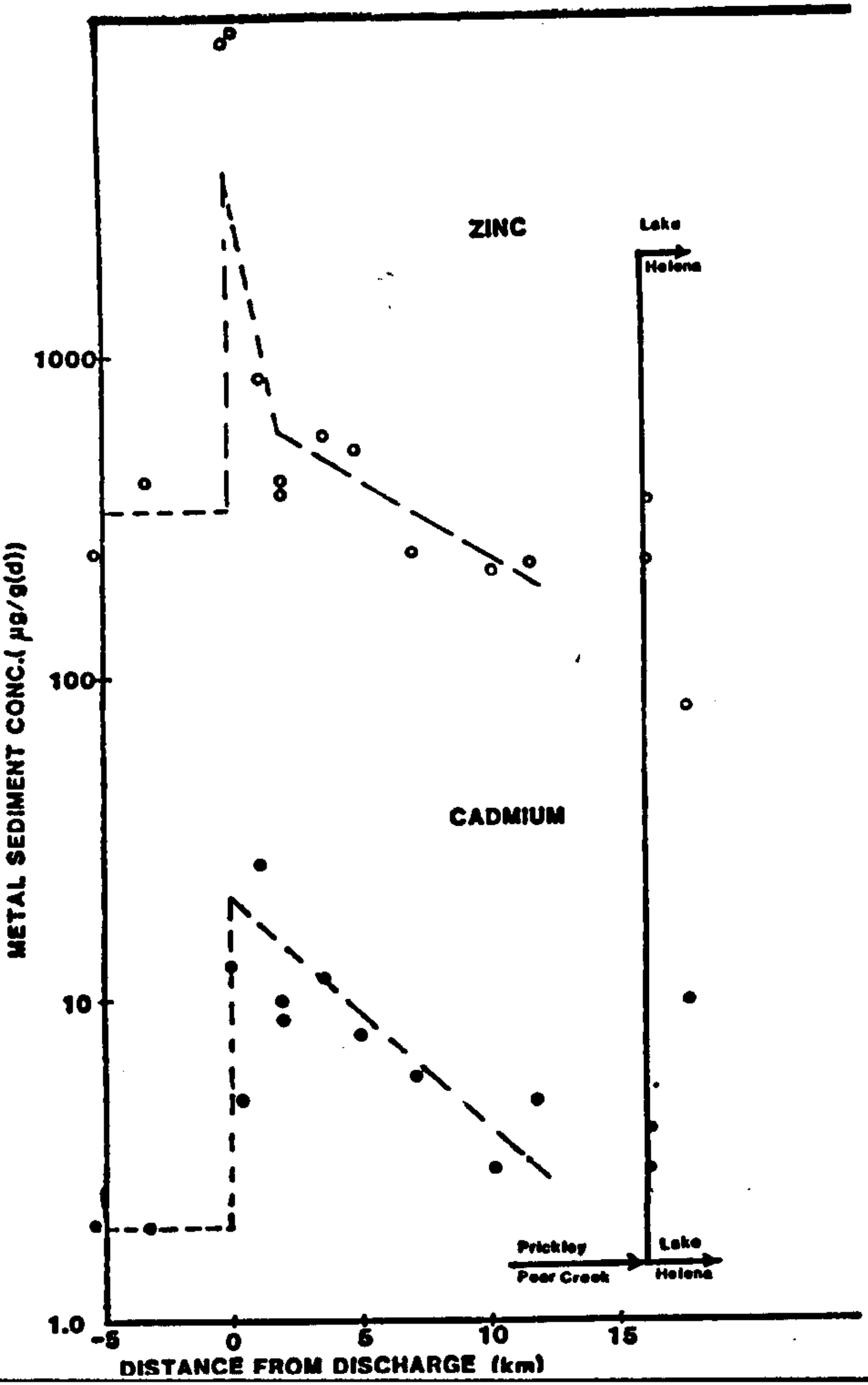
f_d = fraction in diss. form $= (1 + \pi m)^{-1}$

f_p = fraction in part. form $= 1 - f_d$

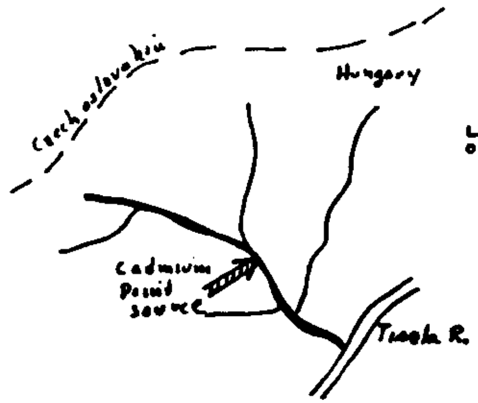
Fig. 3-8 : SCHEMATIC OF IMPACT OF INCREASING TURBIDITY ON ADDITIONAL DOWNSTREAM POINT SOURCE INPUT





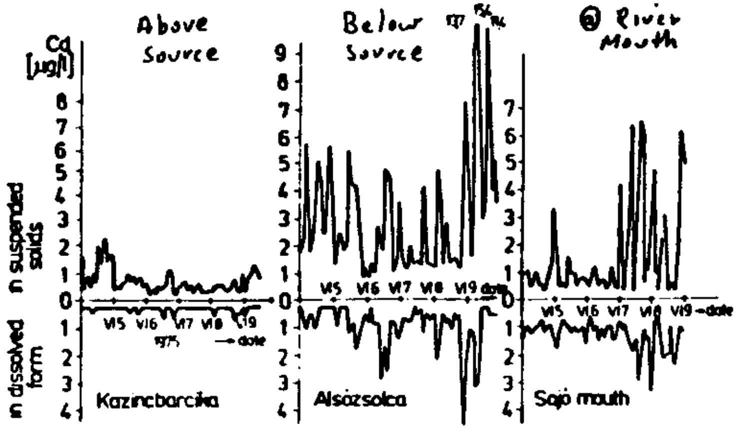


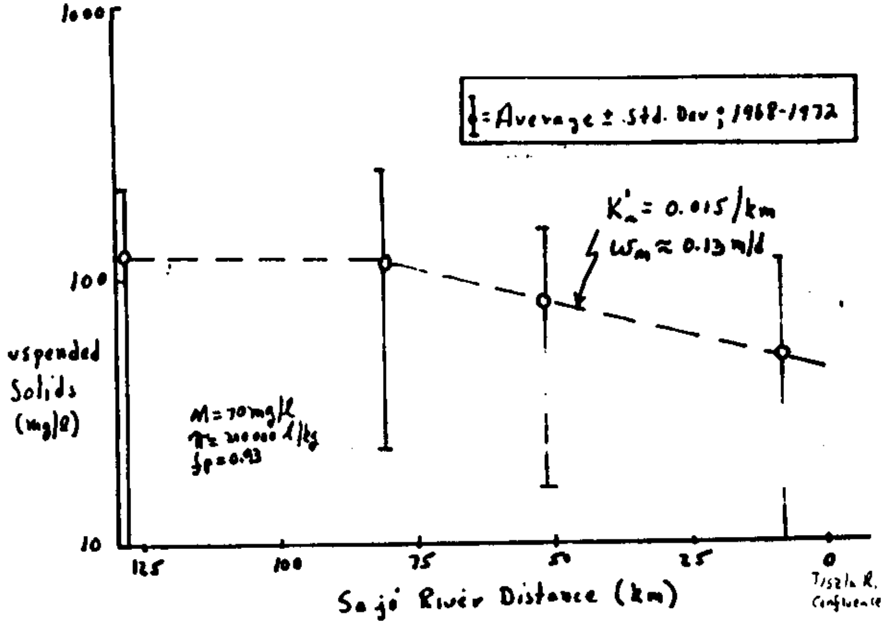
<u>Application</u>: Sajó River, Hungary
(Literáthy and László, 1976)
(Data: Private Communication)



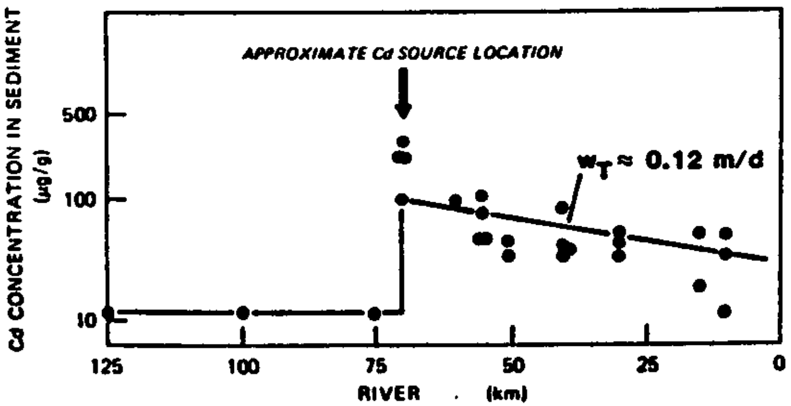
River flow ≈ 10 m³/s → 50 m³/s
River velocity ≈ 0.1 → 0.5 m/s

Temporal Variation - Cadmium, Water Column





For Solids ≈ 70 mg/l, $\pi_{cadmium} \approx 194{,}000$ l/kg & $f_p = 0.93$



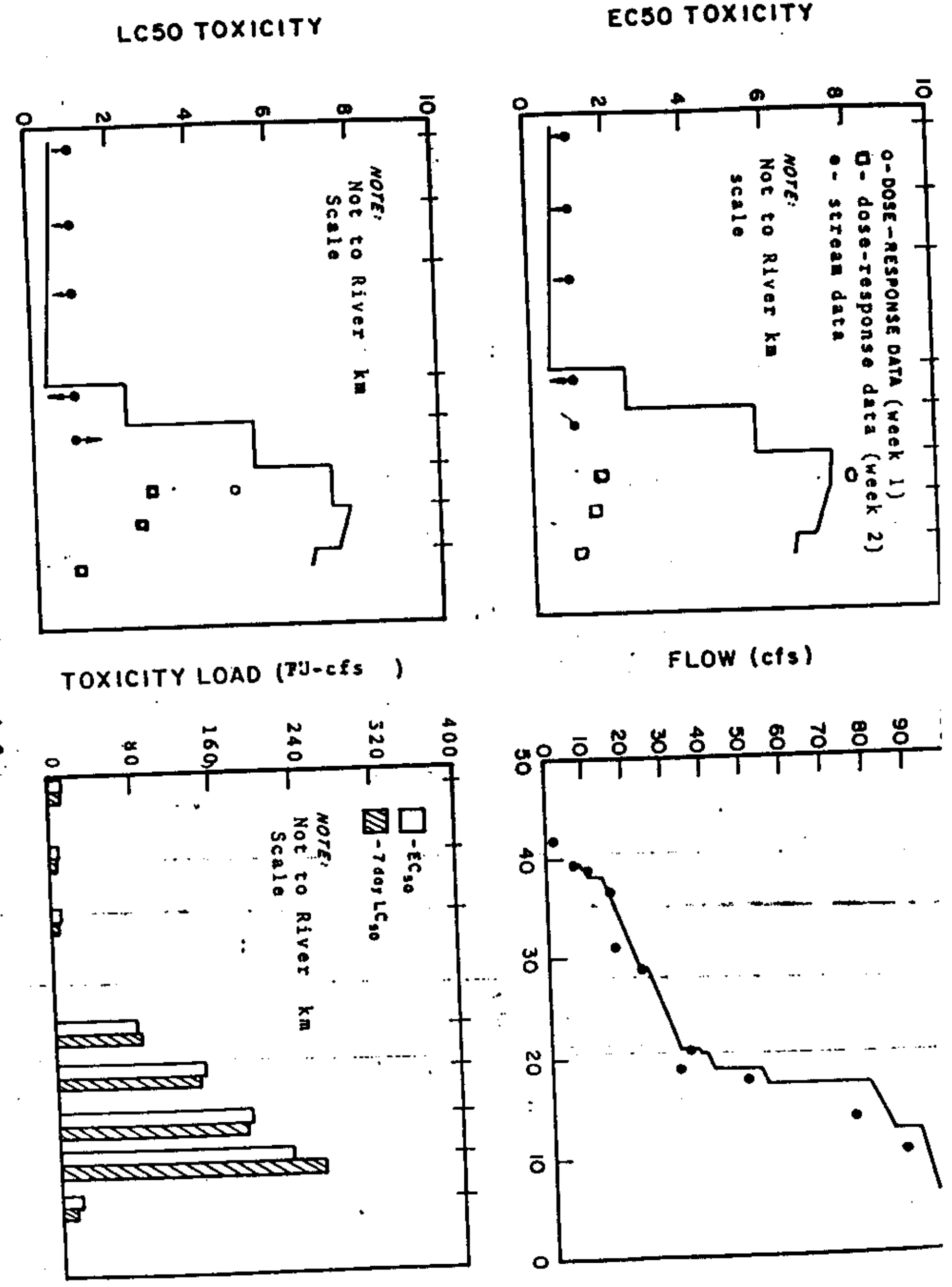
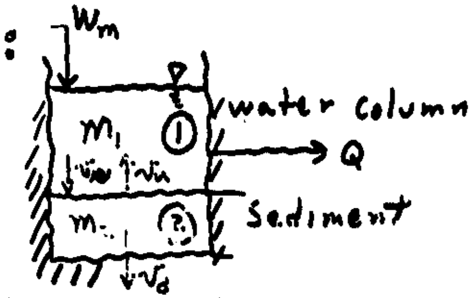


Figure 4-2
Median Toxicity (Additive Case)

(From Di Toro + Hallden 1985)

Mass Balance of Solids

Consider:



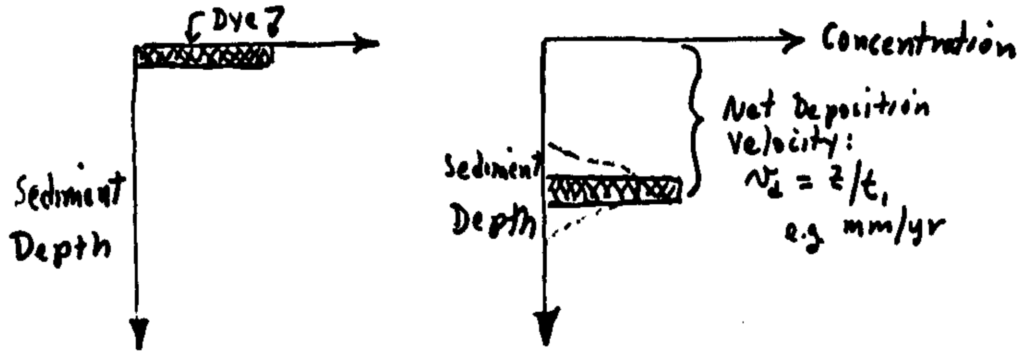
Steady State
Eq for water column:

$$V_1 \frac{dm_1}{dt} = 0 = W_m - Q m_1 \quad \text{T[illegible]}$$
$$- v_s A m_1 \quad \text{settling}$$
$$+ v_u A m_2 \quad \text{Resuspension}$$

Steady State
Eq. for sediment:

$$V_2 \frac{dm_2}{dt} = 0 = v_s A m_1 \quad \text{Settling}$$
$$- v_u A m_2 \quad \text{Resuspension}$$
$$- v_d A m_2 \quad \text{Net Deposition (Burial)}$$

Net Deposition:



@ time $t=0$ @ time $t = t_1$

Solve sediment eq + substitute into water column eq:

$$0 = W_m - Q m_1 - v_n A m_1$$

where

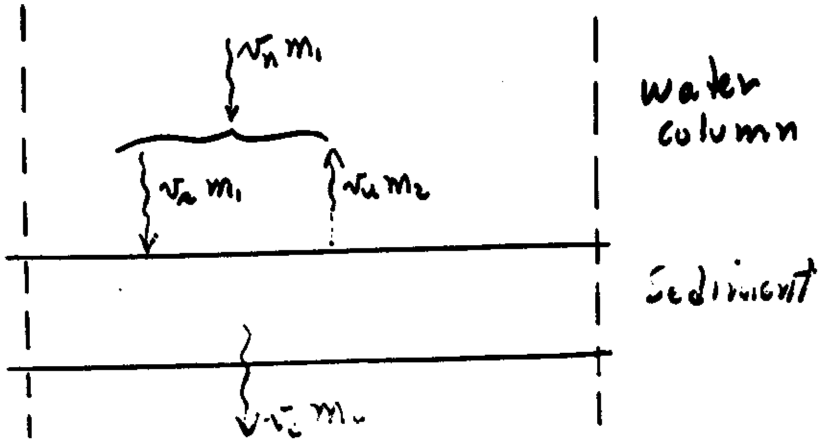
$$v_n = v_s v_d / (v_u + v_d)$$

= net loss of solids from water column

∴ water col. solids is

$$m_1 = \frac{W_m}{Q + v_n A}$$

Mass Balance Around Sediment



∴ at steady state

$$v_d m_2 = v_n m_1$$

Can obtain net loss of solids from water column, v_n from mass balance eq.

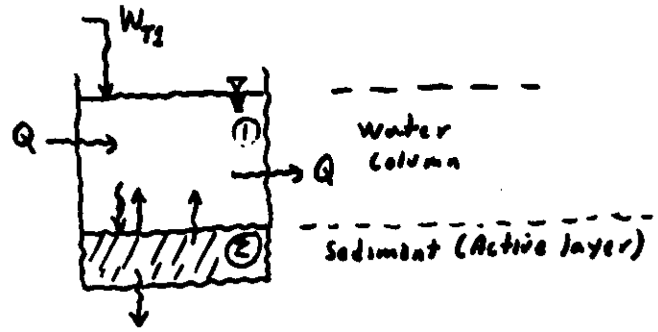
i.e. $v_n = \frac{W_m}{A m_1} - \frac{Q}{A}$

then $v_d = \frac{v_n m_1}{m_2}$ } or measure v_d from sediment traps or tracers

then estimate

$$v_n = \frac{v_d m_2}{m_1}$$

Steady State - Completely Mixed Lake with Sediment Interaction



Water Column: Total Toxicant Mass Balance

$$
\begin{aligned}
V_1 \frac{dc_{T1}}{dt} = 0 = \; & W_{T1} && \text{Input Loads} \\
& + (Q c)_{in} && \\
& - Q c_{T1} && \text{- Mass outflow} \\
& - v_s A f_{p1} c_{T1} && \text{- Settling} \\
& + v_u A f_{p2} c_{T2} && \text{- Resuspension} \\
& + K_f A (f_{d2} c_{T2}/\phi_2 - f_{d1} c_{T1}) && \text{- Sed. Diffusion} \\
& - K_1 V_1 c_{T1} && \text{- Decay, photolysis} \\
& + K_l A (c_g/H_e - f_{d1} c_{T1}) && \text{- Atmospheric exchange}
\end{aligned}
$$

where $K_1 = K_{d1} f_{d1} + K_{p1} f_{p1}$

Sediment:

$$V_2 \frac{dc_{T2}}{dt} = 0 = v_s A f_{p1} c_{T1} \quad \text{- Settling}$$

$$- v_u A f_{p2} c_{T2} \quad \text{- Resuspension}$$

$$+ K_f A (f_{d1} c_{T1} - f_{d2} c_{T2}/\phi_2) \quad \text{- Sediment Diffusion}$$

$$- v_d A f_{p2} c_{T2} \quad \text{- Net sedimentation}$$

$$- K_2 V_2 c_{T2} \quad \text{- Sed. decay}$$

where $K_2 = K_{d2} f_{d2} + K_{p2} f_{p2}$

Sediment concentration usually measured on particulate solids basis, i.e.

$$\underset{\frac{\mu g \text{ Tox}}{g \text{ (dry) sed.}}}{r_2} = \frac{f_{p2} c_{T2}}{m_2}$$

Solution of Water Column & Sediment Equations

$$c_{T1} = \frac{W_{Ta}}{q + v_T}$$

where

W_{Ta} = Areal loading rate of chemical $[M_T / L^2\text{-}T]$

v_T = overall net loss of chemical $[L/T]$

$q = \frac{Q}{A_s}$ = Depth / Detention time

$$v_T = \left(K_1' + \beta \frac{r_2}{r_1} (K_2' + K_a')\right) H_1 = v_{Td} + v_{Ta}$$

where:

$K_1' = (K_{d1} + k_a/H_1) f_{d1} + K_{p1} f_{p1}$

$K_2' = K_{d2} f_{d2} + K_{p2} f_{p2}$

$K_a' = v_d f_{p2} / H_2$

$\beta = (m_2 H_2 f_{p1}) / (m_1 H_1 f_{p2})$

$v_{Td} = K_1' H_1$

$v_{Ta} = \beta \frac{r_2}{r_1} (K_2' + K_a') H_1$

and

$$\frac{r_2}{r_1} = \frac{\text{sed. part. conc.}}{\text{water col. part. conc.}}$$

$$= \frac{(v_u + v_d) f_{p2} + K_f (\theta_2 / \theta_1) f_{d2} / \phi_2}{(v_u + v_d) f_{p2} + K_f f_{d2}/\phi_2 + K_2' H_2}$$

Level #1 Analysis

For: Zero decay of toxicant in sediment

Equal partition coefficients in water column + sediment

Then:

$$r_2 = r_1 \quad \text{(Sed. conc. = Particulate water col. Conc.)}$$

and

$$v_T = (k_\ell + K_{d1} H_1) f_{d1} + (v_n + K_{p1} H_1) f_{p1}$$

Dissolved Loss — Particulate Loss: Net settling + decay

For zero decay in water column:

$$v_T = f_{p1} v_n$$

$$= (\text{fraction particulate}) \cdot (\text{Net solids Loss Rate})$$

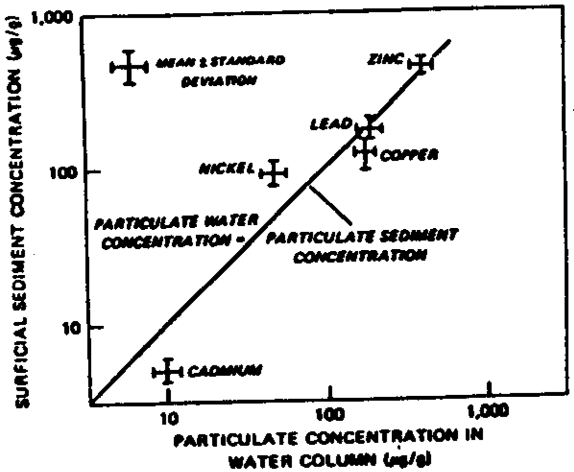
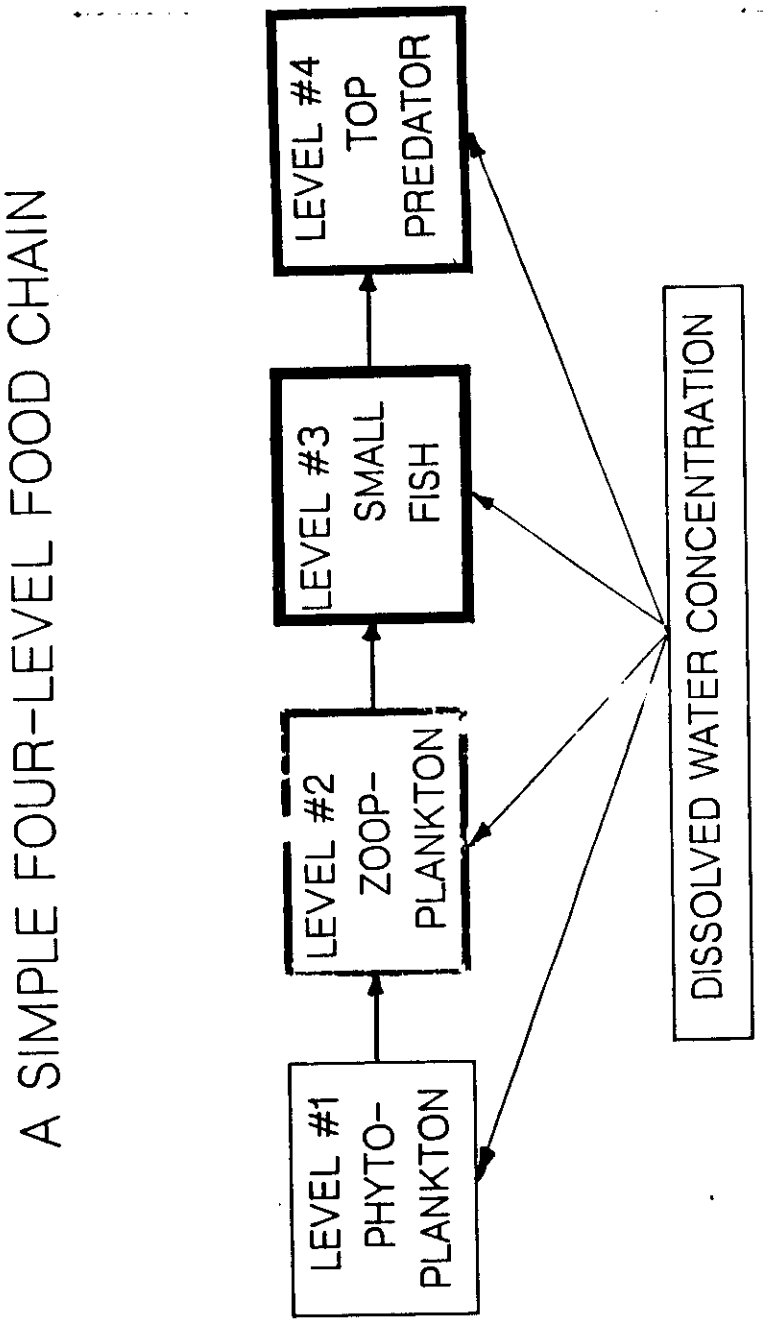
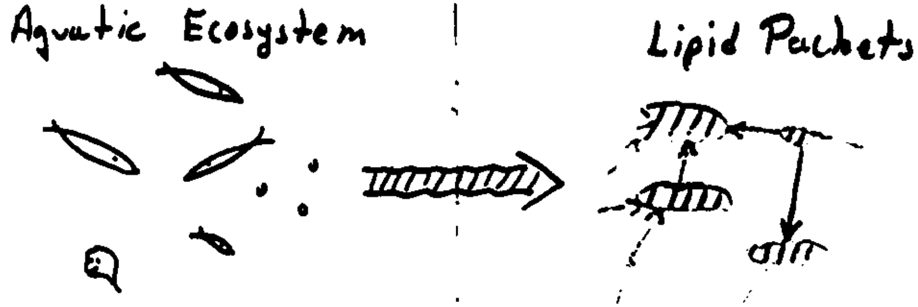
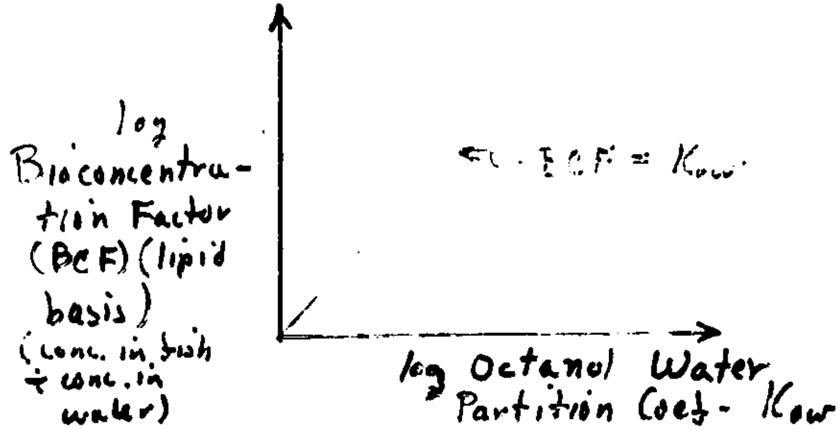


Fig. 4. Lake Ontario correlation of particulate metals concentration on suspended solids in water column and particulate metals concentration in surficial sediments (calculated from data in Nriagu, et al., 1981)



Equilibrium Partitioning of Organic Chemicals





∴ Conc. in Fish = $[K_{ow} \cdot \text{fraction lipid}] \cdot$ water conc.

$\nu = K_{ow} \cdot l \cdot c$

$\left(\frac{\mu g}{g(\text{wet})}\right)$

Accumulation from Water Only

Bioconcentration Factor (BCF)

On whole body basis:

$$\frac{dv'}{dt} = k_u w c - K v'$$

v' = μg chem / organism = $v w$

w = weight - g(lipid)

v = conc. on lipid basis (μg / g(lip))

k_u = uptake rate - $\frac{\text{liter}}{\text{d - g(lip)}}$

K = excretion rate - day^{-1}

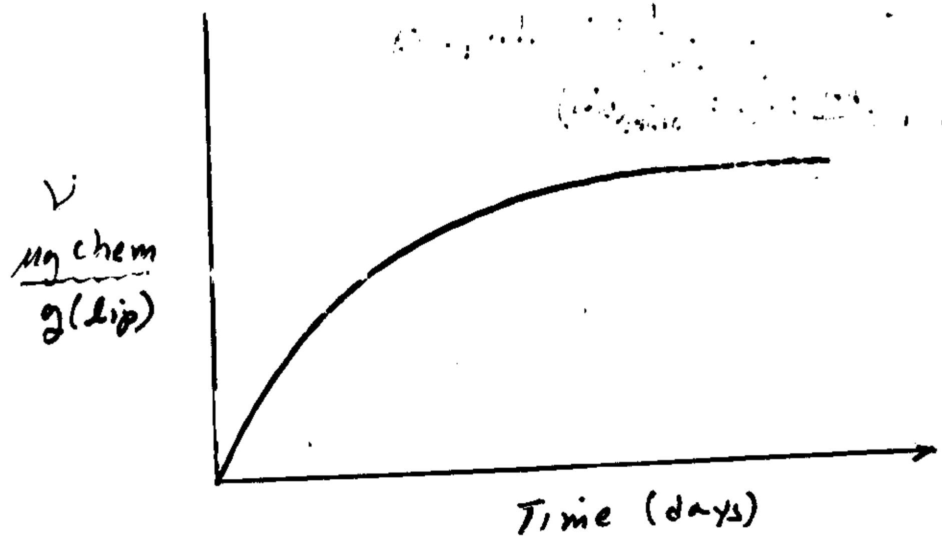
On concentration basis:

$$\frac{dv}{dt} = k_u c - (K + G) v$$

G = net growth rate of

1. Solution:

$$v = \frac{k_u c}{K+G}\left(1 - \exp(K+G)t\right)$$



Net Growth Rate given by

$$G \approx 0.01\, w^{-0.2}$$

Excretion Rate

For $G = 0$: (Lab conditions)

Assume $N_w = K_{ow} = \frac{k_u}{K}$

$$\therefore K = \frac{k_u(w, E, K_{ow}, lip.)}{K_{ow}}$$

For $G \neq 0$: (Field conditions)

$$K' = K + G$$

$$= \frac{k_u}{K_{ow}} + .01\,w^{-0.2}$$

Uptake rate: $k_u = \beta \cdot \frac{r}{(DO)} \cdot E$

$\beta = \frac{\text{diffusivity of chemical}}{\text{diffusivity of oxygen}}$

r = respiration rate of fish (g oxy / g(w) - d)

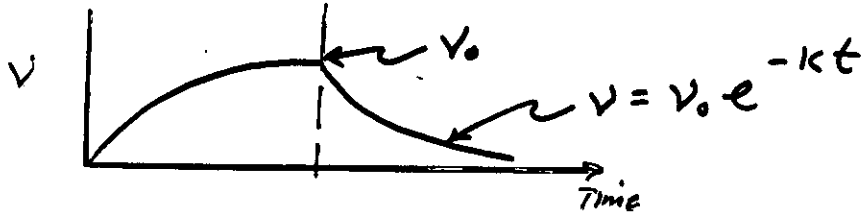
Do = diss. oxygen

E = membrane (gill) transfer efficiency

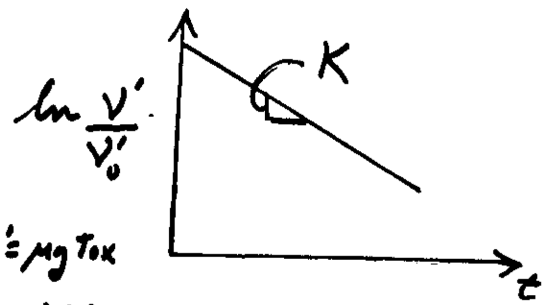
Excretion rate:

$$K \approx 1400\, K_{ow}^{-(.85 \rightarrow 1.00)}$$

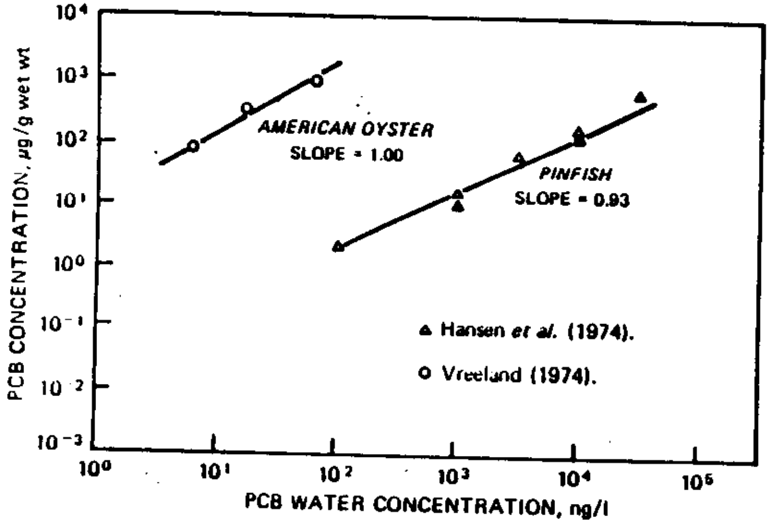
Depuration of chemical

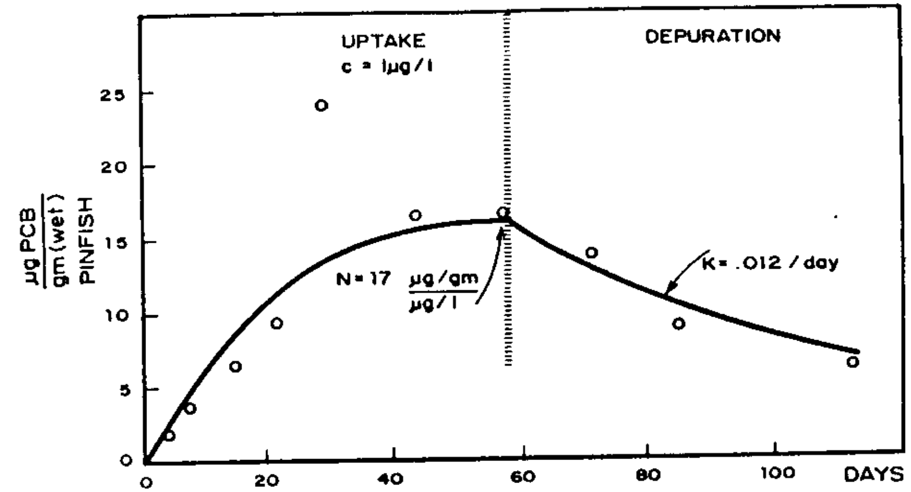


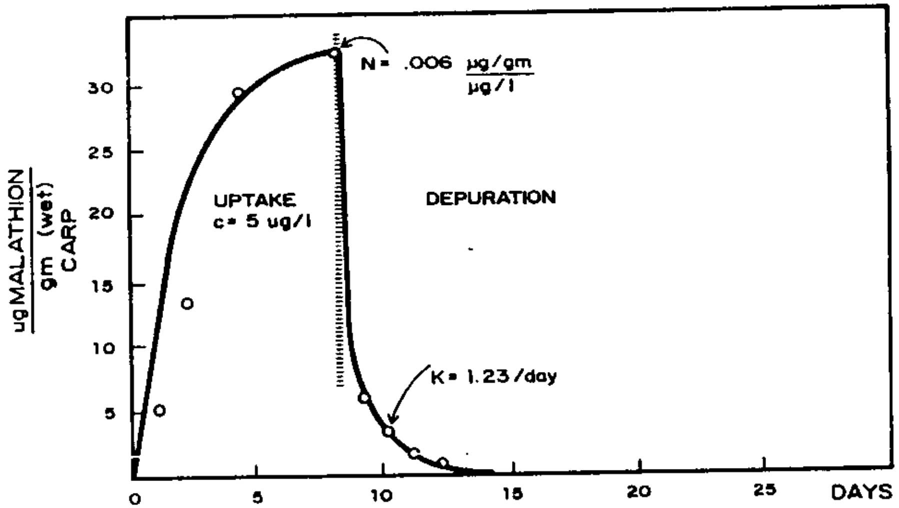
or



where $\nu' = \mu g$ Tox $= \nu w$







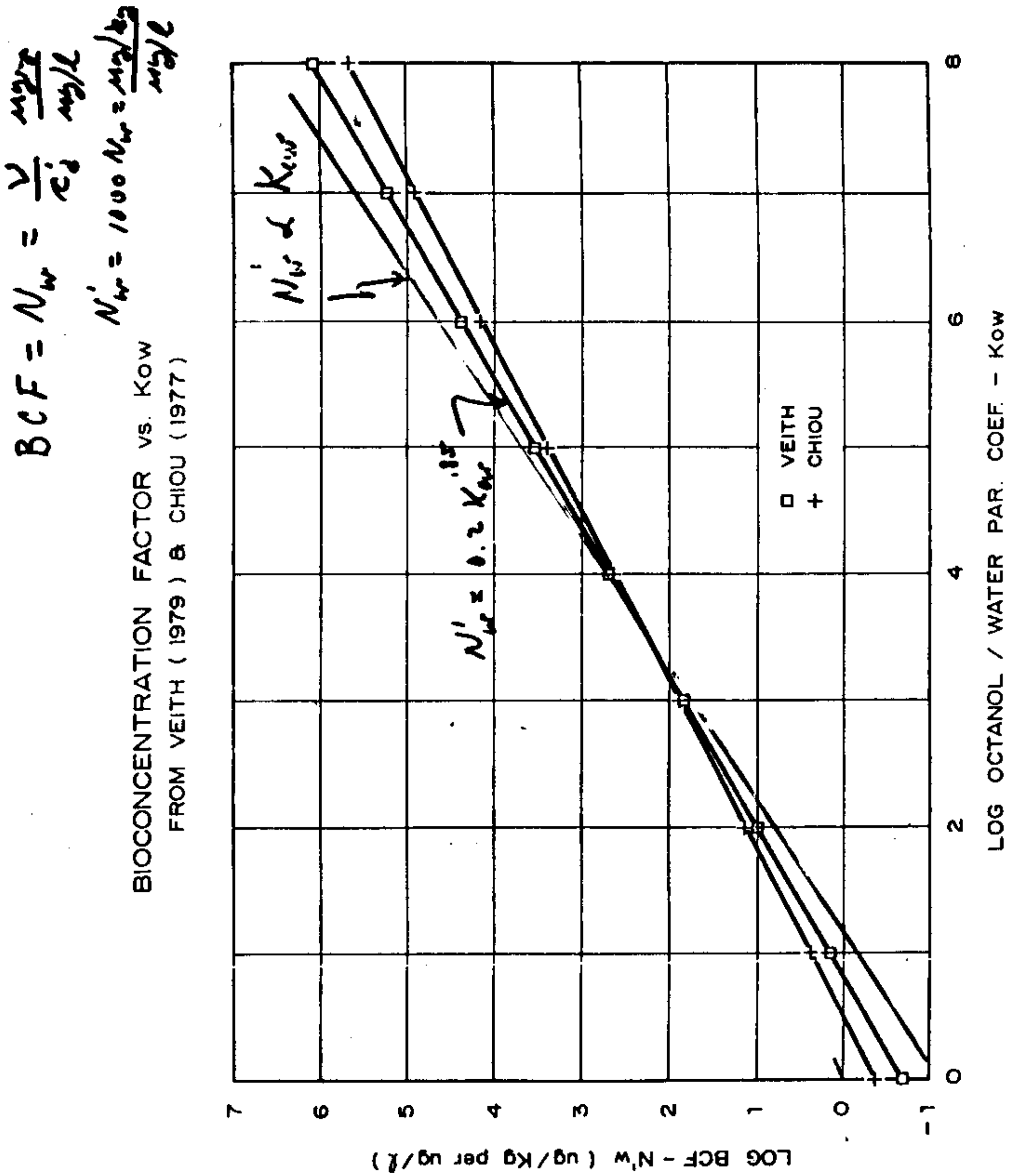
BIOCONCENTRATION AND DEPURATION FOR : a) PCB (Hansen et al, 1974) AND b) MALATHION (Bender, 1964)

@ equilibrium $\nu = \frac{k_u}{K} c$

or define the bioconcentration factor as

$$N_w = \frac{\nu}{c} = \frac{k_u}{K}$$

or $N_w' = 1000\, N_w$



Examples

	N_w' ℓ/kg(w)	K 1/day
Diazinon	152	0.8
Heptachlor	4,600	0.08
Dieldrin	52,000	0.01

For organic lipophylic chemicals, relate N_w' to octanol/water partition coef.

ex. Veith: $N_w' = 0.2\, K_{ow}^{.85}$

Also good to express on a lipid basis i.e. $\frac{\mu g}{g(w)} \cdot \frac{g(w)}{g(lipid)} = \frac{\mu g}{g(lipid)}$

Food Chain Biomagnification

Uptake of chemical from food depends on:

1) How much food is eaten
2) concentration of chemical in the food
3) Assimilation efficiency of chemical ingested

$$\frac{d\nu}{dt} = k_u c - K'\nu + \alpha C \nu_{food}$$

where: $K' = K + G$

α = toxicant assim. eff.

C = consumption rate of food (g (prey) / g (predator) - day)

Solution @ steady state:

$$\nu = \frac{k_u c}{K'} + \left(\frac{\alpha C \nu_{food}}{K'}\right)$$

= food chain biomagnification

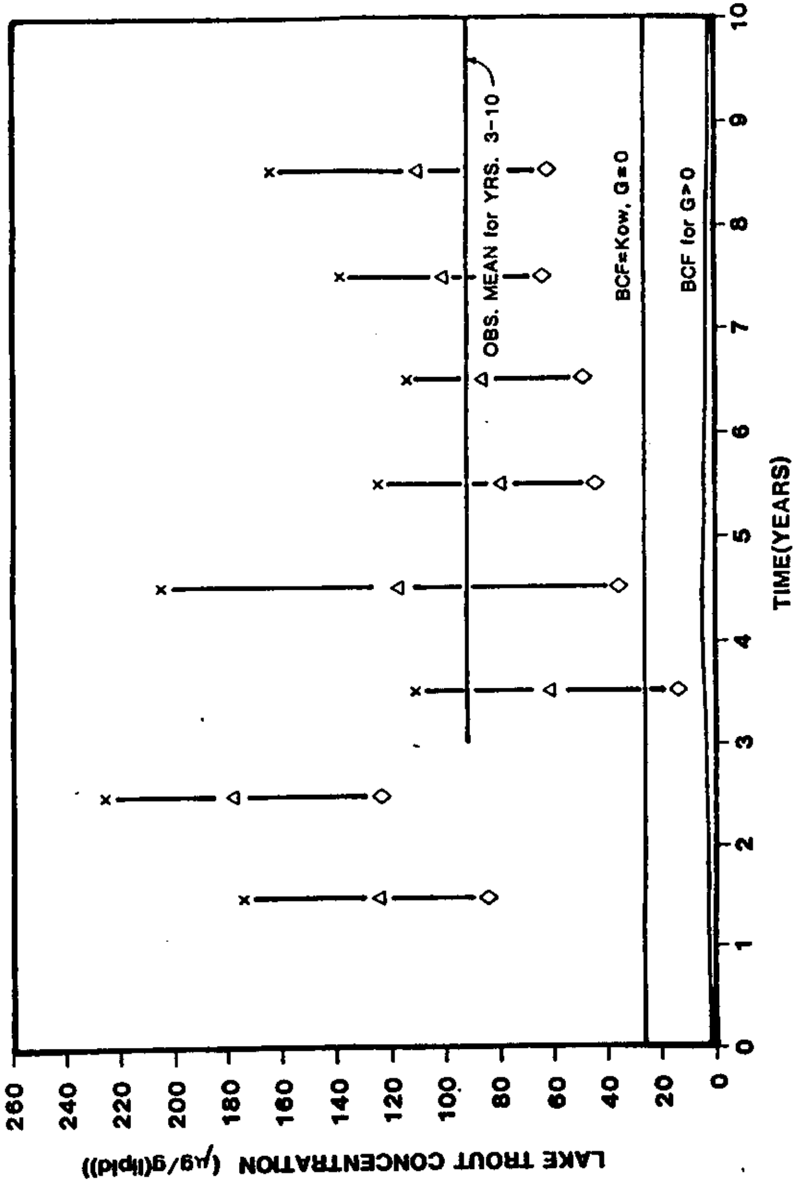


Figure 7. Comparison of observed Lake Michigan lake trout PCB data (lipid normalized) to calculated concentrations from water uptake only (from (12), mean ± 1s

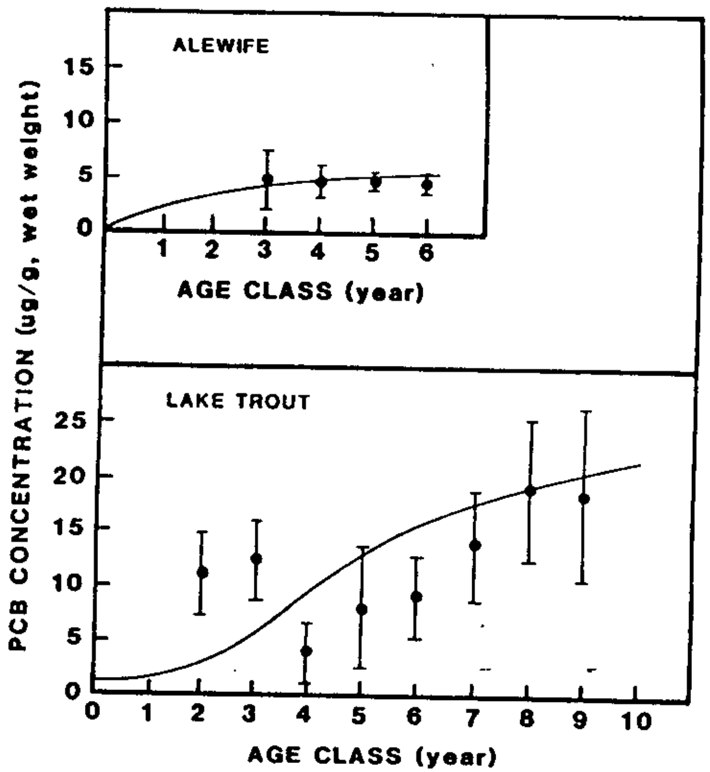


Figure 1. Comparison between observed and calculated PCB concentrations in alewife and lake trout

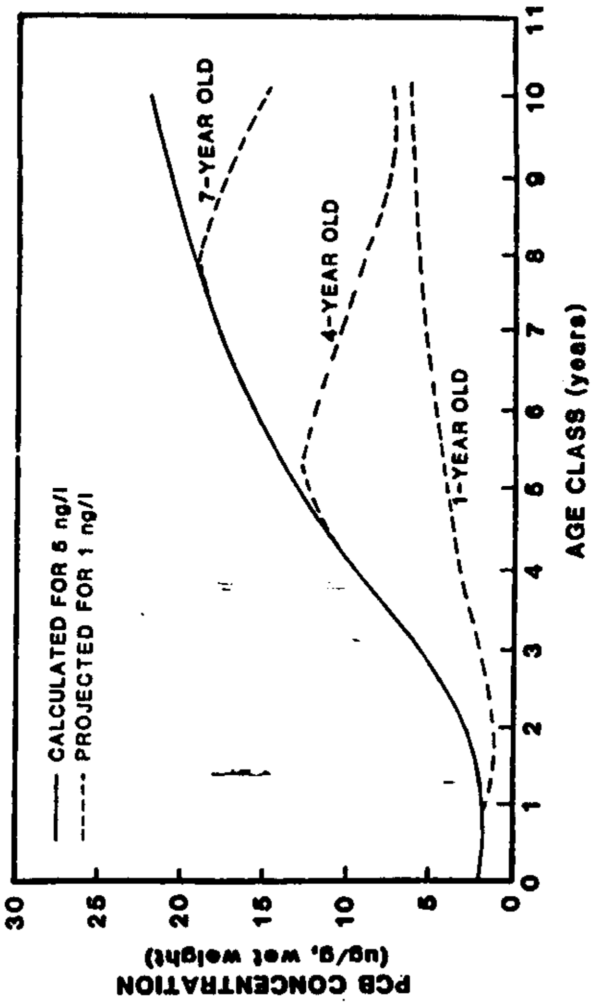
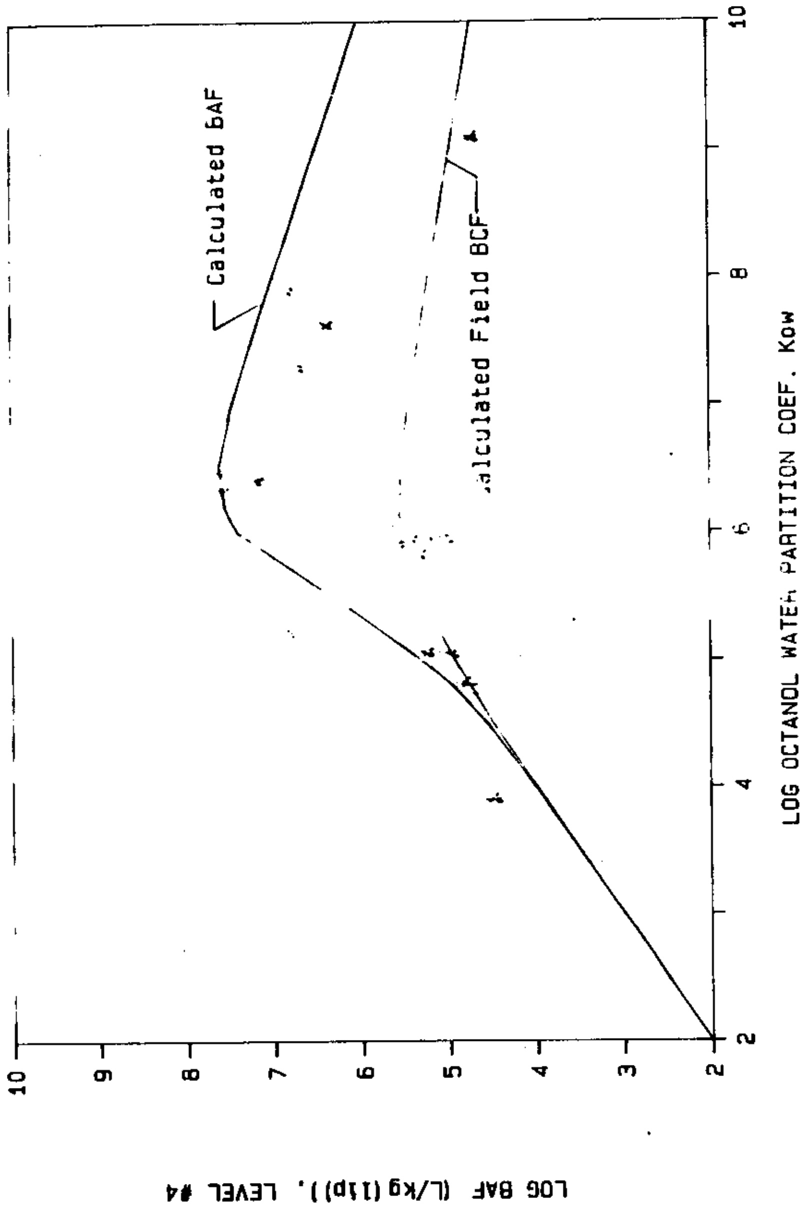
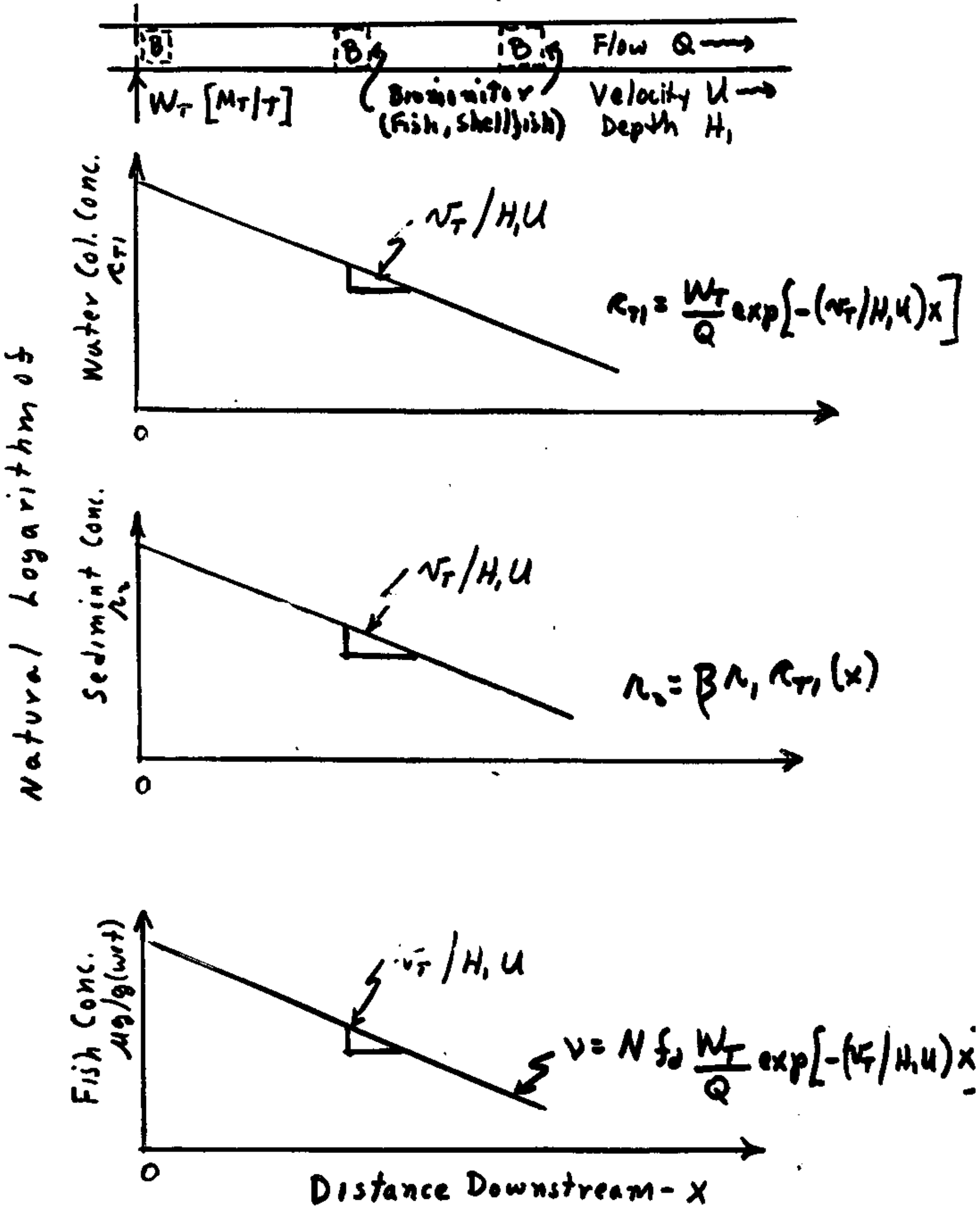


Figure 2. Projected response of different age lake trout to a 5-fold decrease in dissolved PCB concentration



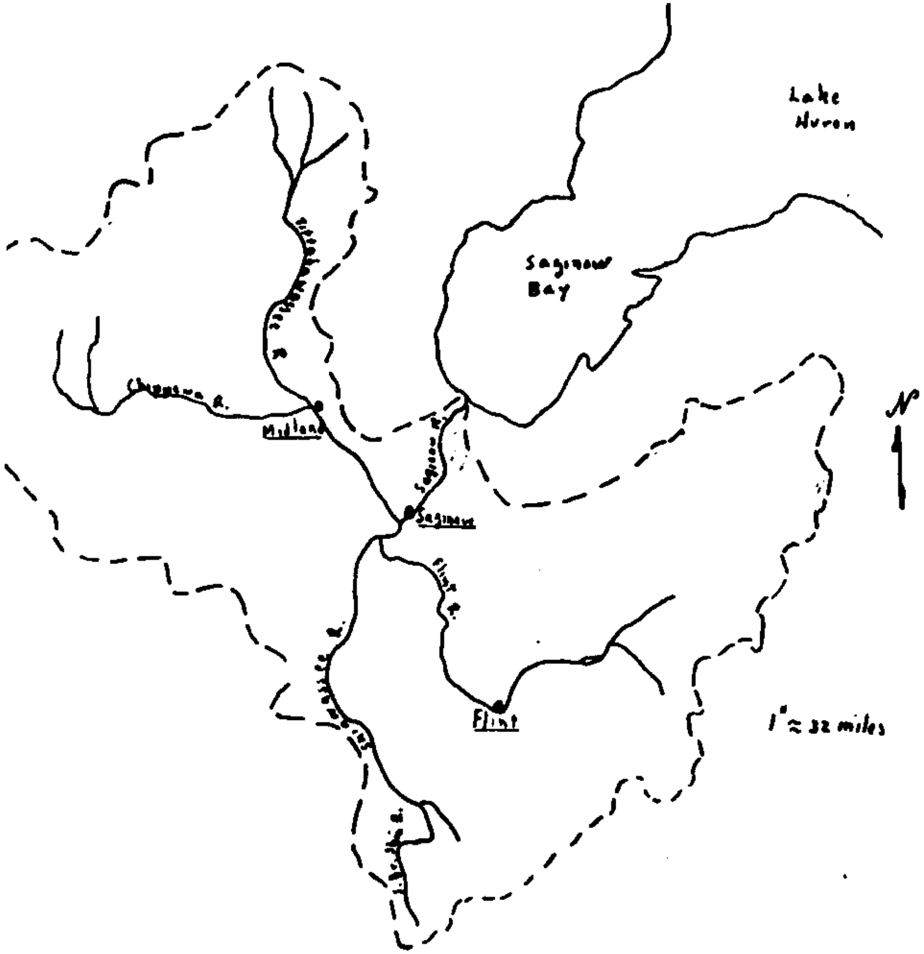


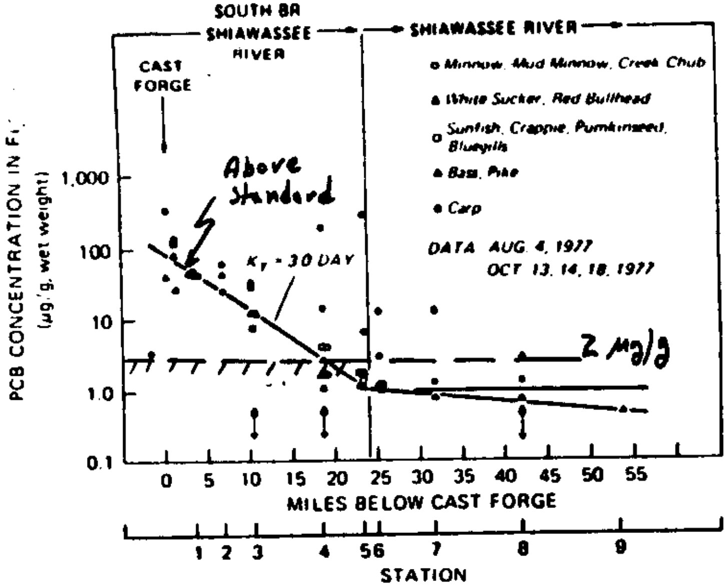
$$r_{T1} = \frac{W_T}{Q} \exp\left[-(\nu_T/H_1 U)x\right]$$

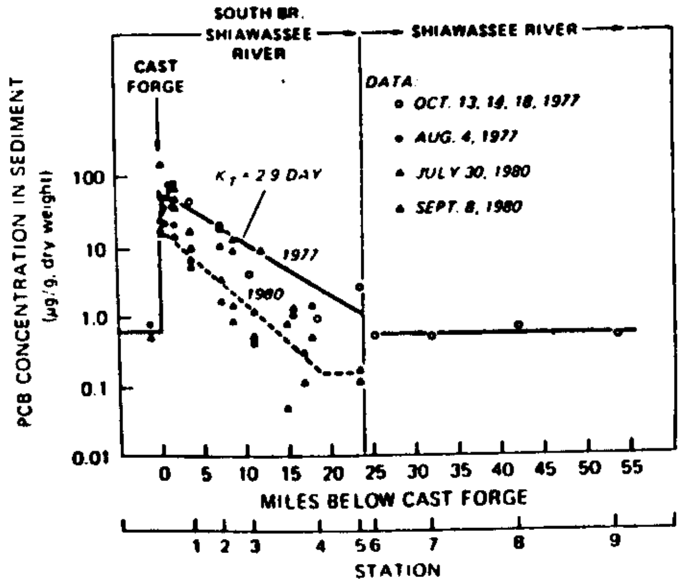
$$r_2 = \beta r_1 r_{T1}(x)$$

$$\nu = N f_d \frac{W_T}{Q} \exp\left[-(\nu_T/H_1 U)x\right]$$

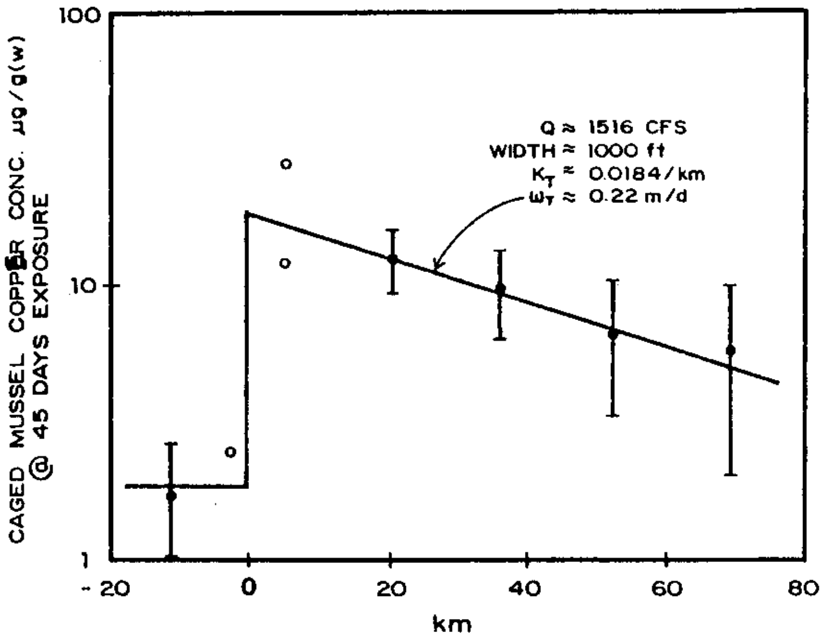
Application: PCB in Shiawassee River, Mich.







VARIATION OF COPPER CONCENTRATION IN CAGED MUSSELS, QUADRULA quadrula, Muskingum R. Set 1973, Data from Foster and Bates (1978)



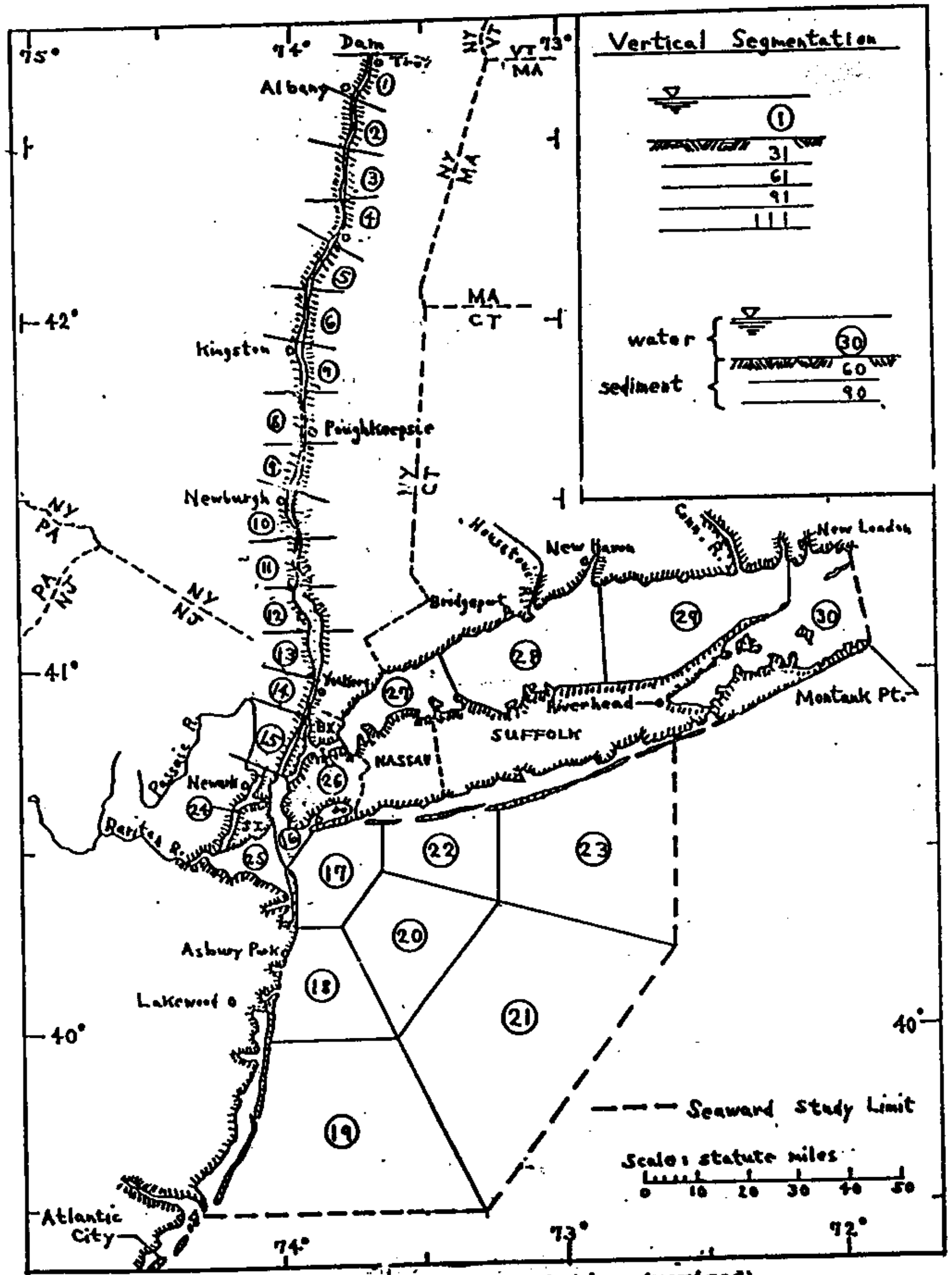
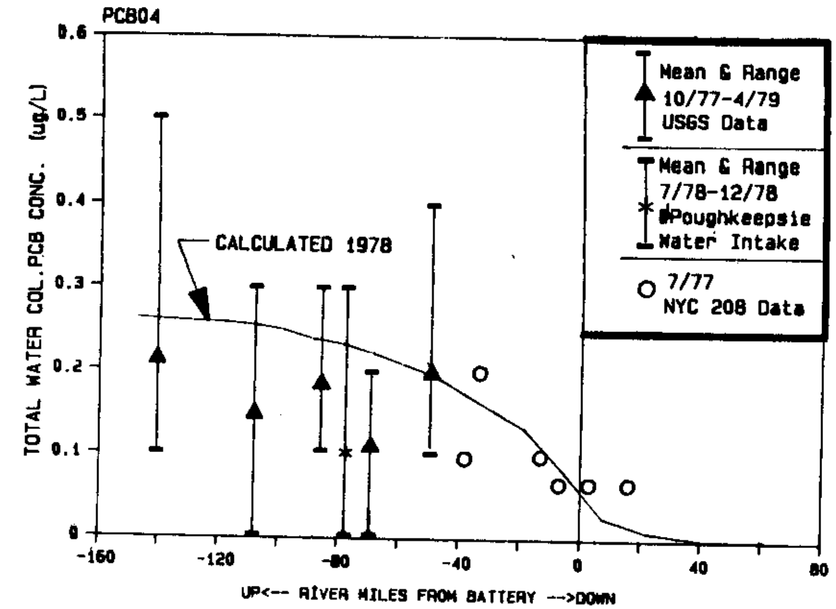
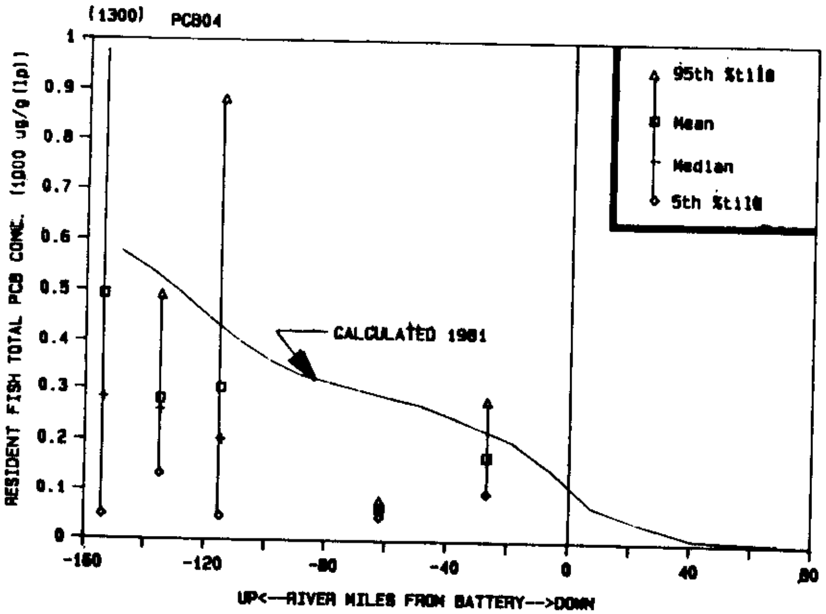
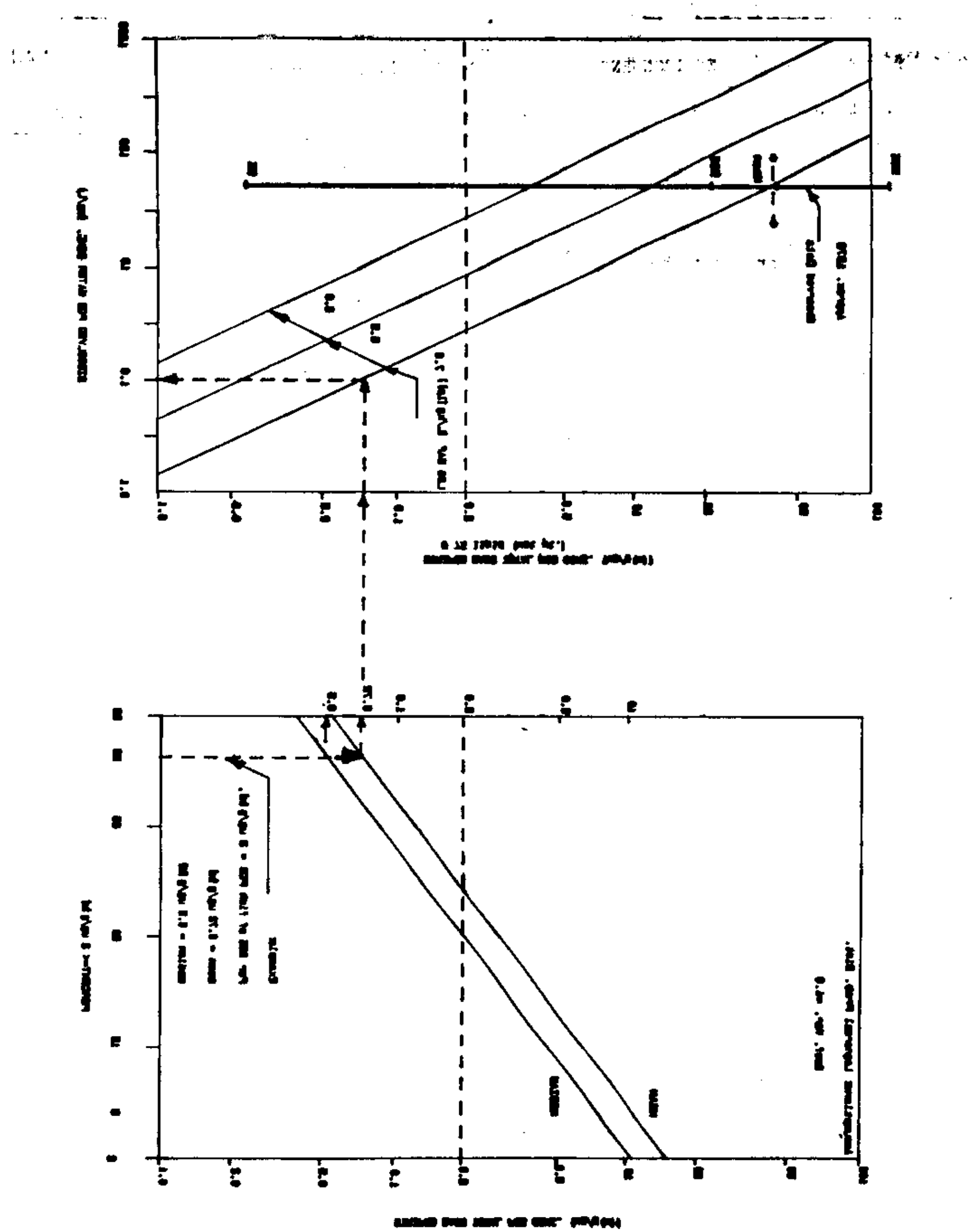
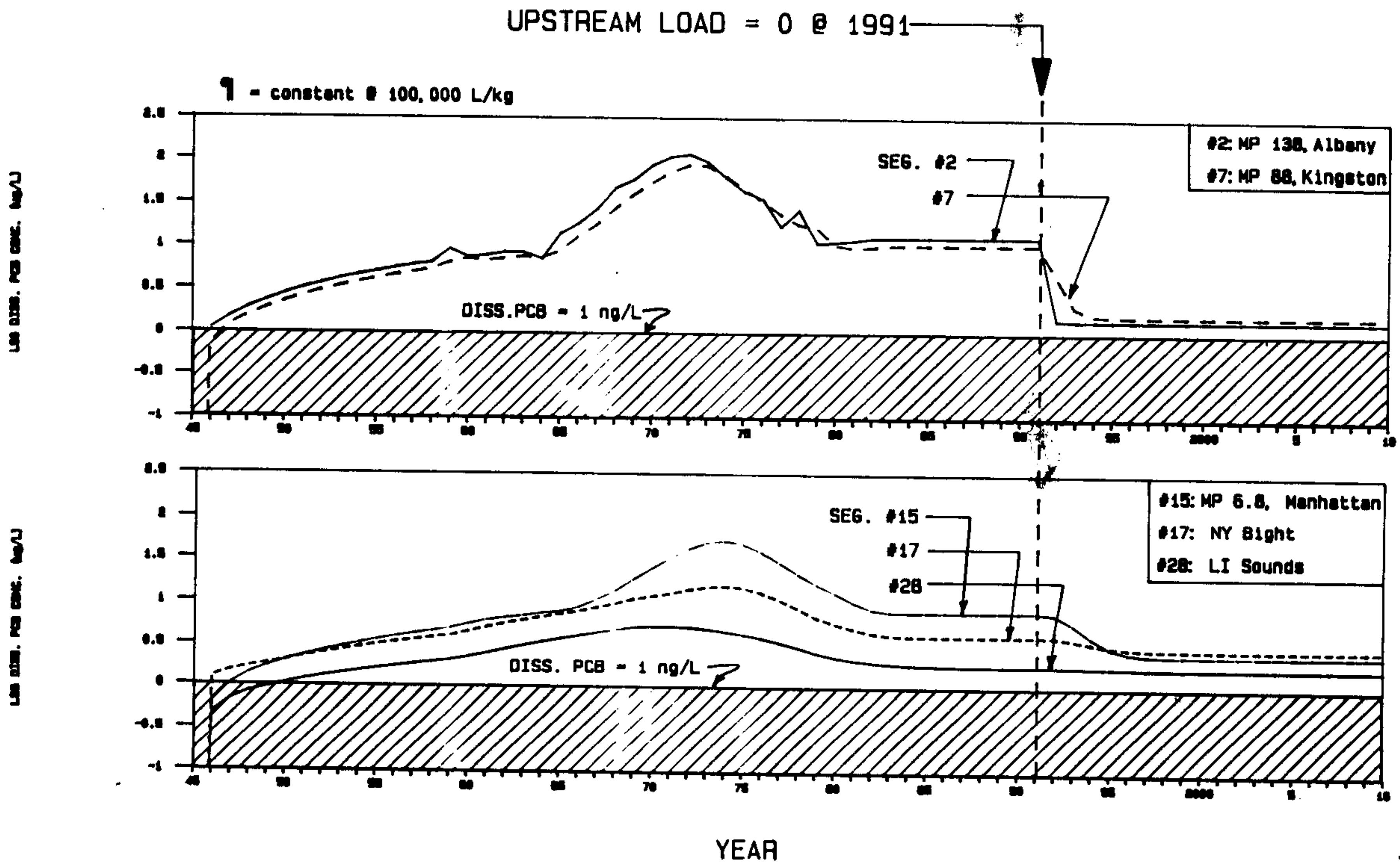


Figure 8. Model Segmentation (revised)


PCB04
Mean & Range
10/77-4/79
USGS Data
Mean & Range
7/78-12/78
@Poughkeepsie
Water Intake
7/77
NYC 208 Data
CALCULATED 1978
TOTAL WATER COL.PCB CONC. (ug/L)
UP<-- RIVER MILES FROM BATTERY -->DOWN
0.6
0.5
0.4
0.3
0.2
0.1
0
-160
-120
-80
-40
0
40
80


(1300)
PCB04
95th %tile
Mean
Median
5th %tile
CALCULATED 1981
RESIDENT FISH TOTAL PCB CONC. (1000 ug/g (lp))
UP<--RIVER MILES FROM BATTERY-->DOWN
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-160
-120
-80
-40
0
40
80




UPSTREAM LOAD = 0 @ 1991
¶ = constant @ 100,000 L/kg
SEG. #2
#7
#2: MP 138, Albany
#7: MP 88, Kingston
DISS.PCB = 1 ng/L
SEG. #15
#17
#28
#15: MP 6.8, Manhattan
#17: NY Bight
#28: LI Sounds
DISS. PCB = 1 ng/L
YEAR