UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

SMR.940 - 19

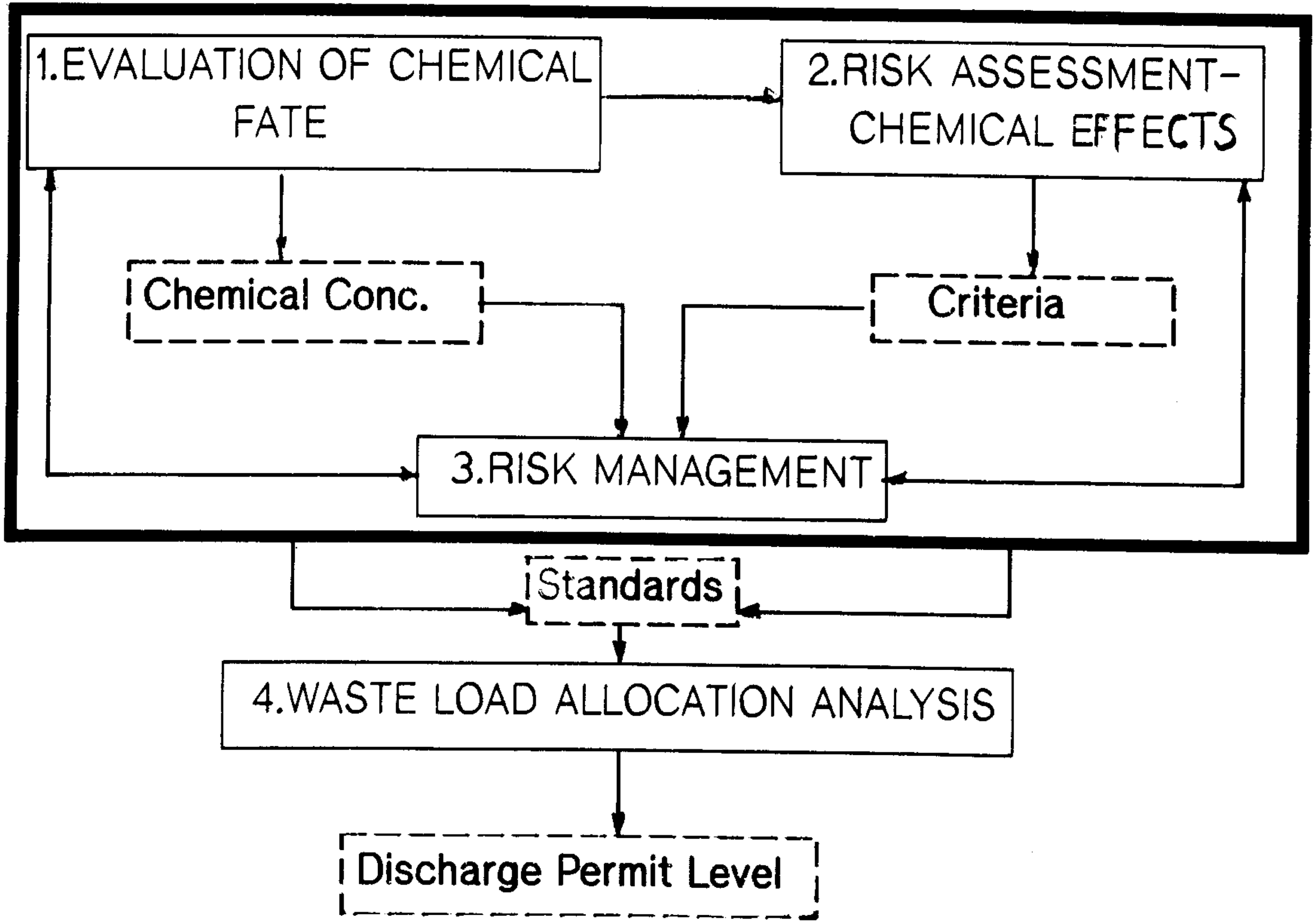
THIRD AUTUMN WORKSHOP ON MATHEMATICAL ECOLOGY

(14 October - 1 November 1996)

"Modelling of Toxics in Lakes and Biocumulation and Aquatic Food Chains"

Robert V. Thomann
Environmental Engineering Department
Manhattan College
New York, N.Y. 10471
U.S.A.

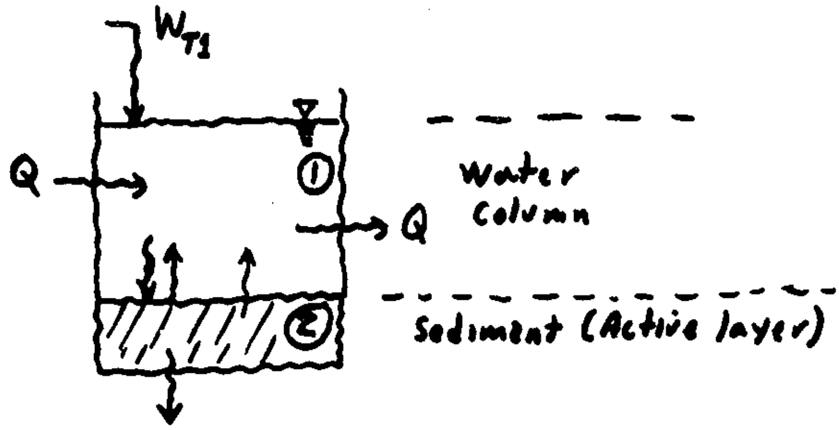
These are preliminary lecture notes, intended only for distribution to participants.


1.EVALUATION OF CHEMICAL FATE
2.RISK ASSESSMENT-CHEMICAL EFFECTS
Chemical Conc.
Criteria
3.RISK MANAGEMENT
Standards
4.WASTE LOAD ALLOCATION ANALYSIS
Discharge Permit Level

Where is chemical to be found?

Water Column:	Free dissolved form Sorbed to suspended particulates (Sorbed to colloids, DOC)
Sediment:	Sorbed to sediment solids Free dissolved form in interstitial water (Sorbed to DOC)
Food Web:	In muscle, organs, lipid of fish and other aquatic organisms
Atmosphere:	Gaseous phase Sorbed to particulates Dissolved in precipitation

Steady State - Completely Mixed Lake
with
Sediment Interaction



Water Column: Total Toxicant Mass Balance

$$V_1 \frac{dc_{T1}}{dt} = 0 = W_{T1}$$

$$+ (Q\,c_T)_{in} \quad \text{} \Big\} \text{ Input Loads}$$

$$- Q\,c_{T1} \quad - \text{ Mass outflow}$$

$$- v_s A f_{p1} c_{T1} \quad - \text{ Settling}$$

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

$$+ K_f A \left(f_{d2} c_{T2}/\phi_2 - f_{d1} c_{T1} \right) - \text{ Sed. Diffusion}$$

$$- K_1 V_1 c_{T1} \quad - \text{ Decay, photolysis}$$

$$+ K_l A \left(c_g / H_e - f_{d1} c_{T1} \right) \quad - \text{ Atmospheric exchange}$$

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

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

$$r_2 = \frac{f_{p2} c_{T2}}{m_2}$$

$\frac{\mu g \text{ Tox}}{g \text{ (dry) sed.}}$

$$f_{d1} = \frac{1}{1 + \pi_1 m_1} \qquad f_{p1} = 1 - f_{d1}$$

$$f_{p2} = \frac{\pi_2 m_2}{1 + \pi_2 m_2} \qquad f_{d2} = 1 - f_{p2}$$ (small, but not zero)

Steady State Solution of Water Column & Sediment Equations

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

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

$q = Q/A$ = Depth / Detention Time

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

$\therefore$ If v_T is known, calculate c_{T1}

Also: Let $\frac{r_2}{r_1} = \delta$ (dry wt basis)

$$r_2 = \delta r_1 \; ; \; \frac{r_1}{c_d} = \Pi_1$$

$$\therefore \frac{r_2}{c_d} = \delta \Pi_1$$

For organic carbon normalization:

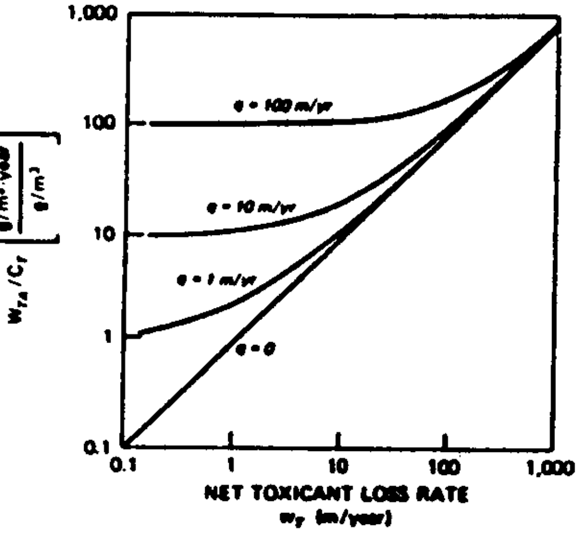
$$\frac{r_2}{c_d} \left(= \Pi_{wa} \left(L/kg(oc)_a \right) \right) = \frac{\delta f_{oc1} \Pi_1}{f_{oc2}}$$

Organic chem:

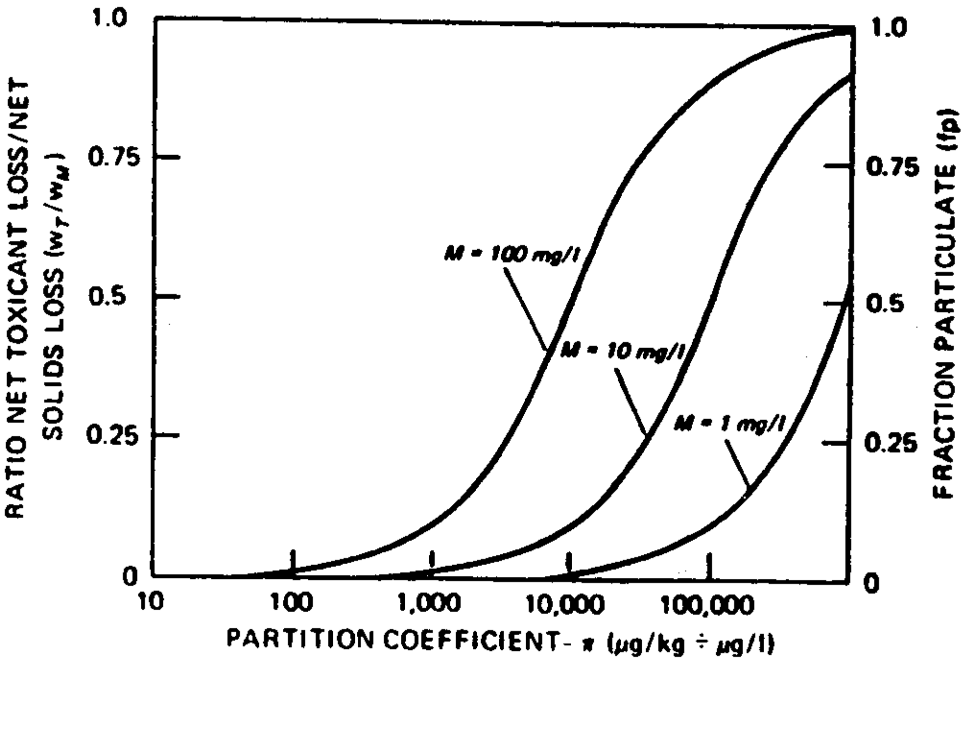
$$\underset{(L/kgoc.)}{\Pi_1} = \frac{K_{ow}}{1 + f_{ocw} K_{ow} m_1 / 1.4}$$

3-15

General Case - Completely Mixed Lake, Steady State



Special Case - Volatilization & decay = 0; $\pi = \pi_s$



6.

From water col. + sediment eqs.:

$$v_T = v_{Td} + v_{Ta}$$

v_{Td} = dissolved chem. loss

$$= (\underbrace{K_{d1} H_1}_{\text{decay, etc.}} + \underbrace{k_\ell}_{\text{vol-atilization}}) f_{d1}$$

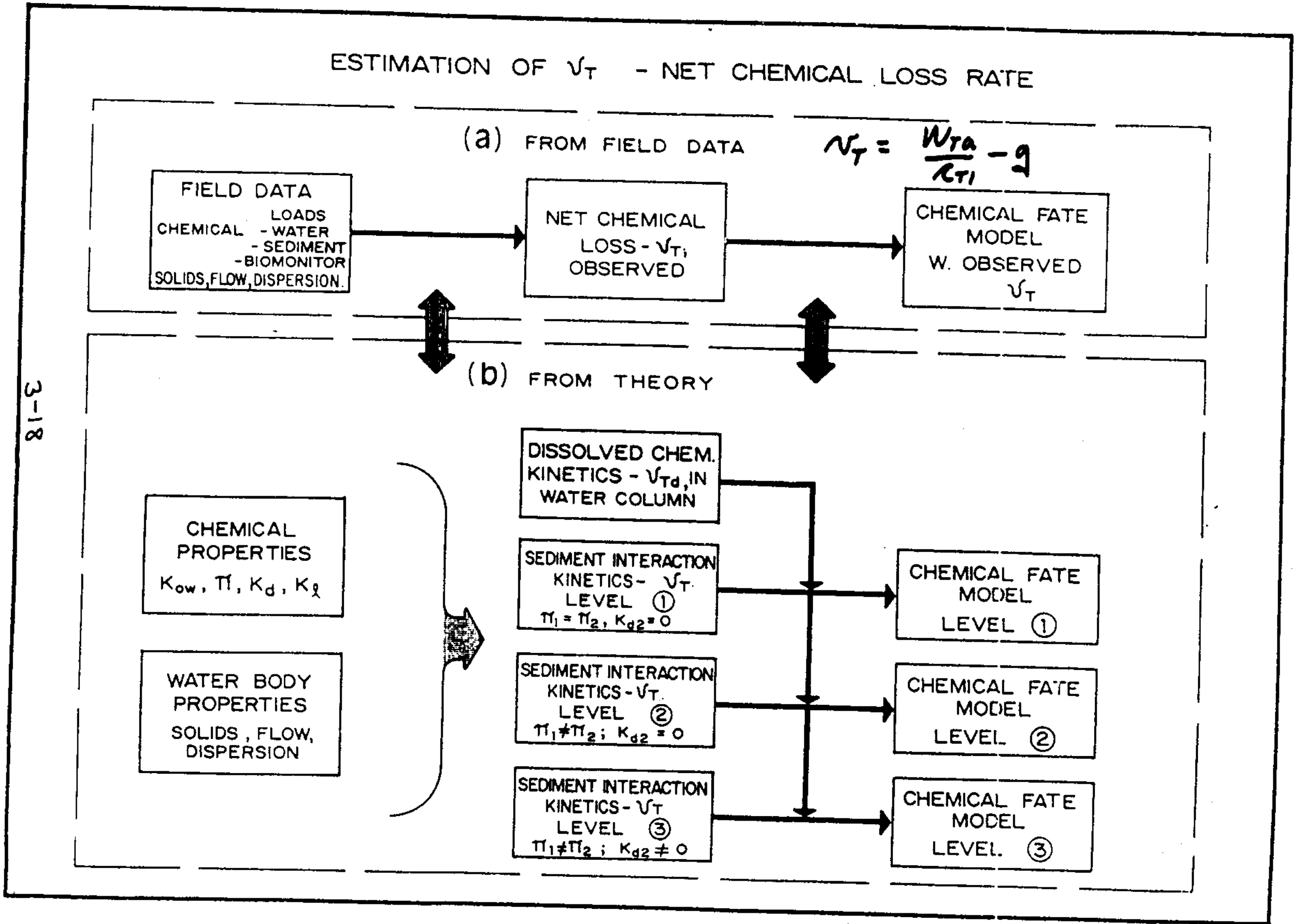
v_{Ta} = loss due to sediment interaction

$$= v_n \eta' \left[1 + \frac{m_2 (K_{d2} f_{d2} H_2)}{m_1 v_n} \right]$$

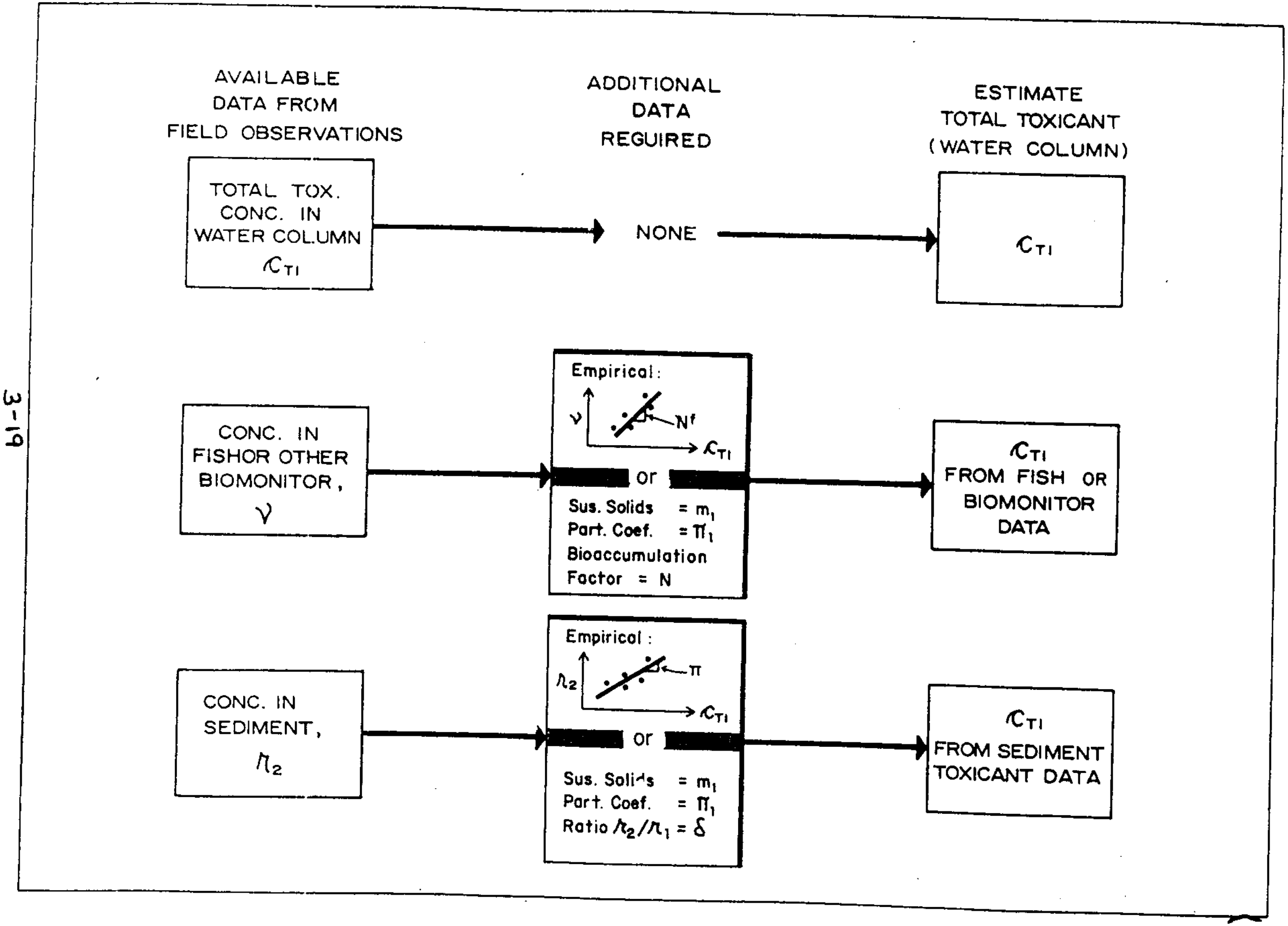
where $$\eta' = \frac{v_a f_{p1} + K_f f_{d1}}{v_a + f_{d2} (m_2/m_1)(K_f + K_{d2} H_2)}$$

Also: $$\frac{r_2}{r_1} = \delta = \frac{(v_u + v_d) f_{p2} + K_f (\pi_2/\pi_1) f_{d2}/\phi_2}{(v_u + v_d) f_{p2} + K_f f_{d2}/\phi_2 + K_{d2} f_{d2} H_2}$$

$$\left[\frac{\mu g}{g(d)_s} \div \frac{\mu g}{g(d)_w} \right]$$


ESTIMATION OF ν_T - NET CHEMICAL LOSS RATE
(a) FROM FIELD DATA
$\nu_T = \frac{W_{Ta}}{c_{T1}} - g$
FIELD DATA
CHEMICAL LOADS
- WATER
- SEDIMENT
- BIOMONITOR
SOLIDS, FLOW, DISPERSION.
NET CHEMICAL LOSS - ν_{T_i} OBSERVED
CHEMICAL FATE MODEL W. OBSERVED ν_T
(b) FROM THEORY
CHEMICAL PROPERTIES
K_{ow}, π, K_d, K_ℓ
WATER BODY PROPERTIES
SOLIDS, FLOW, DISPERSION
DISSOLVED CHEM. KINETICS - ν_{Td}, IN WATER COLUMN
SEDIMENT INTERACTION KINETICS - ν_T LEVEL ①
$\pi_1 = \pi_2$, $K_{d2} = 0$
SEDIMENT INTERACTION KINETICS - ν_T LEVEL ②
$\pi_1 \neq \pi_2$; $K_{d2} = 0$
SEDIMENT INTERACTION KINETICS - ν_T LEVEL ③
$\pi_1 \neq \pi_2$; $K_{d2} \neq 0$
CHEMICAL FATE MODEL LEVEL ①
CHEMICAL FATE MODEL LEVEL ②
CHEMICAL FATE MODEL LEVEL ③

8.


AVAILABLE DATA FROM FIELD OBSERVATIONS
ADDITIONAL DATA REGUIRED
ESTIMATE TOTAL TOXICANT (WATER COLUMN)
TOTAL TOX. CONC. IN WATER COLUMN c_{T1}
NONE
c_{T1}
CONC. IN FISHOR OTHER BIOMONITOR, ν
Empirical:
ν
N^f
c_{T1}
or
Sus. Solids $= m_1$
Part. Coef. $= \pi_1$
Bioaccumulation Factor $= N$
c_{T1} FROM FISH OR BIOMONITOR DATA
CONC. IN SEDIMENT, r_2
Empirical:
r_2
π
c_{T1}
or
Sus. Solids $= m_1$
Part. Coef. $= \pi_1$
Ratio $r_2/r_1 = \delta$
c_{T1} FROM SEDIMENT TOXICANT DATA

Parameters Required for Calculation of Sediment Interaction Loss Rate-v_{Ts}

Level 1	Level 2	Level 3
$\pi_1 = \pi_2$	$\pi_1 \neq \pi_2$	$\pi_1 \neq \pi_2$
$K_{d2} = 0$	$K_{d2} = 0$	$K_{d2} = 0$
Equal partition coef. Zero Sediment Decay	Unequal Partition Coef. Zero Sediment Decay	Unequal Partition Coef. Sediment Decay $\neq$ Zero
v_n	v_n	v_n
π_1	π_1	π_1
m_1	m_1	m_1
	π_2	π_2
	m_2	m_2
	v_s	v_s
	K_f	K_f
		H_2
		K_{d2}

Level #1 Analysis

For: Zero decay of toxicant in sediment
Equal partition coefficients in water column & sediment

Then: $r_2 = r_1$ (Sed. conc. = Particulate water col. conc.)

and

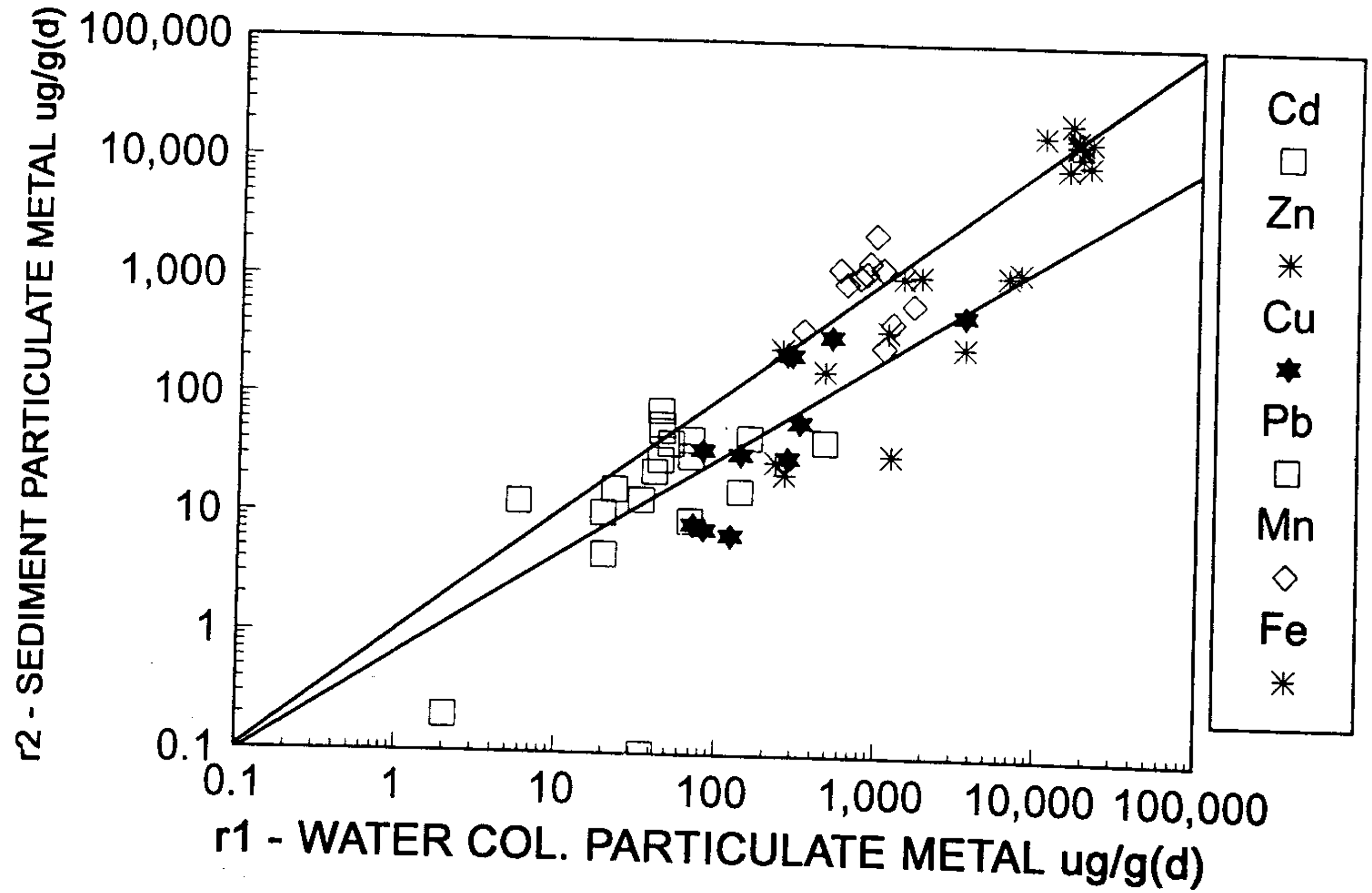
$$v_T = (k_\ell + K_{d1} H_1) f_{d1} + (v_n + K_{p1} H_1) f_{p1}$$

Dissolved Loss — Particulate Loss: Net settling + Decay

For zero decay in water column:

$$v_T = f_{p1} v_n$$

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



South Esk RIVER: REF 645

FIRST APPROXIMATIONS TO CHEMICAL LOAD ALLOCATION
(Completely Mixed Lake)

Approach 1: Minimum Available Data

1. Solids data: Loads, concentration of Sus. Solids or net solids flux to sediment

2. chemical properties: Π, He, decay, etc.

STEPS:

1) From solids balance, obtain v_n, net solids loss rate

Level 1 Analysis ⟹

2) $v_T = (k_l + K_{d1} H_1) f_{d1} + (v_n + K_{p1} H_1) f_{p1}$

3) $(W_{Ta})_{allowable} = (c_T)_{standard} \, (q + v_T)$

$\Pi_2 = \Pi_1$

$K_{d2} = 0$

Approach 2: Minimum Available Data

1. Present chemical loading

2. Present total chemical water column concentration <u>or</u> biomonitor data

Steps:

1) Determine net toxicant loss rate:

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

2)

$$(W_{Ta})_{allowable} = (c_T)_{standard}\,(q + v_T)$$

REFERENCES

Brush, G., 1989. Rates and patters of estuarine sediment accumulation. Lim. and Ocean. 34(7):1235-1246.

Libes, S.M., 1992. An Introduction to Marine Biogeochemistry. J. Wiley & Sons, Inc, New York, 734 pp.

Thomann, R. V. and D. M. D. Toro (1983). "Physico chemical model of toxic substances in the Great Lakes." J. Great Lakes Res. 9(4): 474.

Thomann, R.V. and J.A. Mueller, 1987. Principles of Surface Water Qiality Modeling and Control. Harper & Row, Pub. Co., New York, NY, 644 pp.

Thomann, R. V., J. A. Mueller, et al. (1991). "Model of the fate and accumulation of PCB homologues in Hudson estuary." ASCE, J. Env. Eng. Div. 117(2): 161-178.

Thomann, R. V., W. Merklin, et al. (1993). "Modeling cadmium fate at a superfund site: the impact of bioturbation." Amer. Soc. Civil Engrs. Env. Eng. Div. J. To appear, June 1993.

RATIONALE FOR MODELING BIOACCUMULATION OF CHEMICALS IN AQUATIC FOOD WEBS

HUMAN OR AQUATIC
WILDLIFE

ALLOWABLE DOSE (mg/d) = WATER INTAKE (L/d) * WATER CONC(mg/L)

+ FISH CONSUMP. (kg/d)* FISH CHEMICAL CONC. (mg chem./kg)

BIOACCUMULATION FACTOR-BAF(l/kg) = C(fish)/C(water)

or

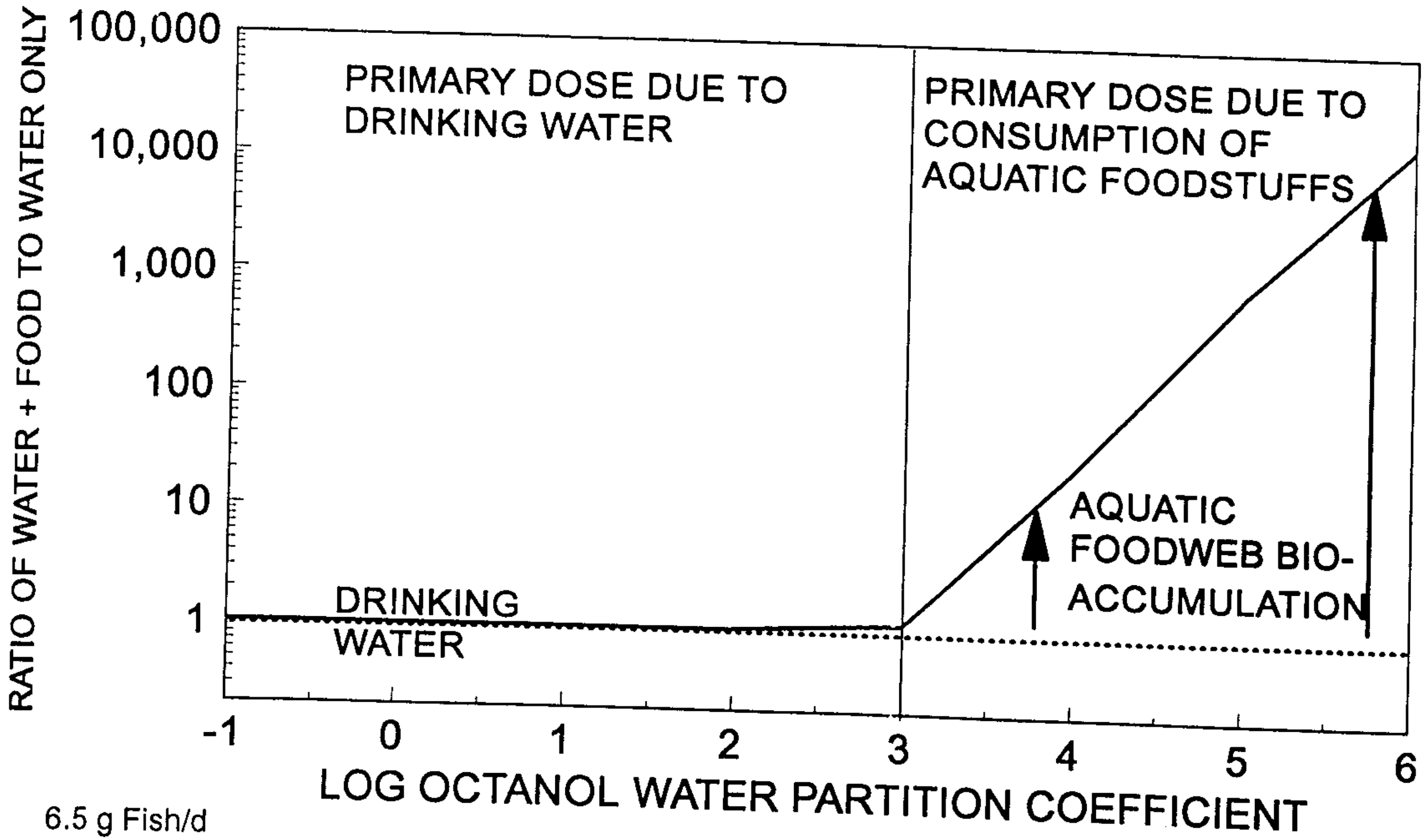
C(fish) = BAF * C(water)

and the required water concentration is then

$$\text{REQUIRED C(water)} = \frac{[\text{ALLOWABLE DOSE}]}{\{\text{Water Intake} + (\text{Fish Consump.} * \text{BAF})\}}$$

IS THE WATER ROUTE OR THE FOOD ROUTE MORE IMPORTANT? DOES THE BAF MATTER?

RELATIVE CHEMICAL DOSE TO HUMANS DUE TO DRINKING WATER AND CONSUMPTION OF CONTAMINATED AQUATIC FOODSTUFFS



6.5 g Fish/d
5% Fish lipid

BASIC STRUCTURE OF BIOACCUMULATION MODELING IN AQUATIC SYSTEMS

ROUTES OF CHEMICAL EXPOSURE:

1. UPTAKE OF "AVAILABLE" CHEMICAL IN WATER COLUMN OR SEDIMENT PORE WATER

2. UPTAKE OF CHEMICAL FROM INGESTION OF CONTAMINATED PREY

3. UPTAKE OF CHEMICAL FROM INGESTION OF CONTAMINATED SEDIMENT

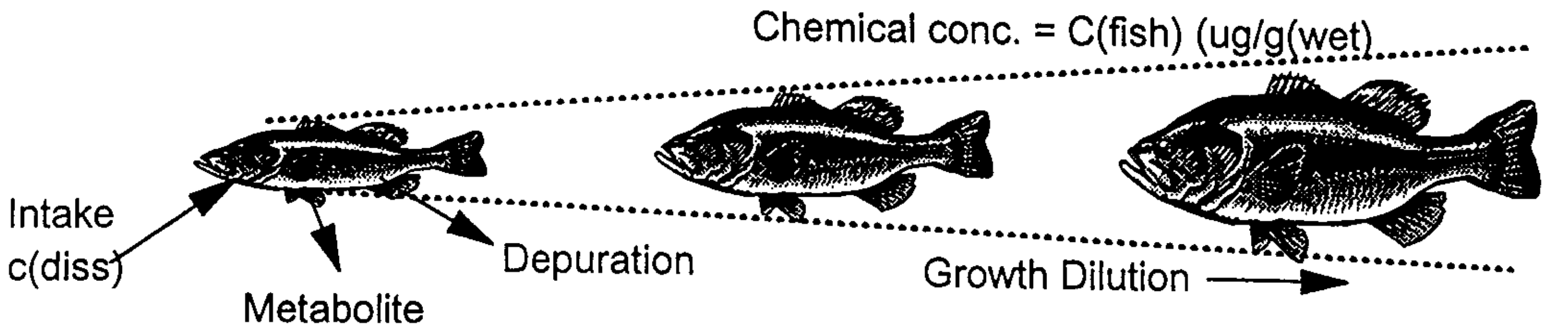
UPTAKE FROM WATER ***ONLY***

BIOCONCENTRATION

CHEMICAL CONCENTRATION IN ORGANISM DUE TO EXPOSURE TO WATER COLUMN, SEDIMENT PORE WATER OR BOTH

DETERMINED BY EXPERIMENT :
NO CONTAMINATED FOOD
CONSTANT WATER CONCENTRATION

ASSUME UPTAKE LINEAR TO WATER CONC.



ug chem/g(wet) per day	=	Intake	-	Depuration	-	Metabolism	-	Growth dilutic
dC(fish)/dt	=	k c(diss)	-	KC(fish)	-	(Km)C(fish)	-	GC(fish)

ug chem/g(wet) per day = Intake - Loss, transformation, dilution routes

$$dC(fish)/dt = kc(diss) - K'C(fish)$$

Continue lab exposure until steady state is reached. Then, intake = losses and

$$C(fish) = kc(diss)/K'$$

Define a <u>BIOCONCENTRATION FACTOR (BCF)</u> as ratio fish conc./diss. water conc. for exposure to water only:

$$BCF = C(fish)/c(diss)$$

NOTE:

1. BCF is an equilibrium ratio for exposure to **water only**
2. In the field, the organism experiences all routes of exposure. Therefore, not possible to measure BCF in the field. BCF is a laboratory determined number.

BIOACCUMULATION

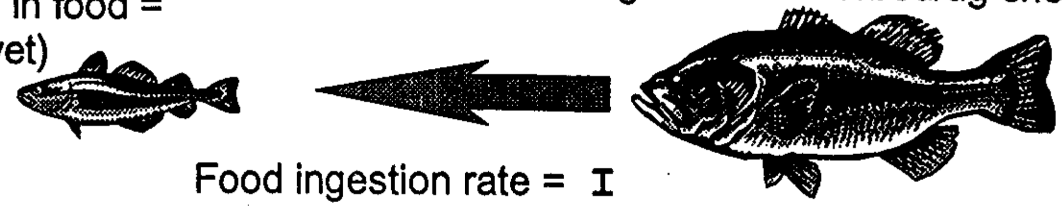
CHEMICAL CONCENTRATION IN ORGANISM DUE TO EXPOSURE TO WATER+CONTAMINATED PREY AND/OR SEDIMENT

GENERALLY A FIELD DETERMINED QUANTITY

CHEMICAL FROM FOOD ADDITIVE TO WATER ROUTE

Chemical assimilation efficiency = e
ug chem. absorbed/ug chem. ingested

Chemical conc. in food =
C(food) (ug/g(wet)



Food ingestion rate = I
(g(prey)/g(predator) per day

ug chem/g(wet) per day	=	Intake	-	Loss	+	Net chemical from food
dC(fish)/dt	=	kc(diss)	-	K'C(fish)	+	e I C(food)

At steady state:

$$C(fish) = BCF c(diss) + g\, C(food)$$

where g = biomagnification ratio = eI/K'

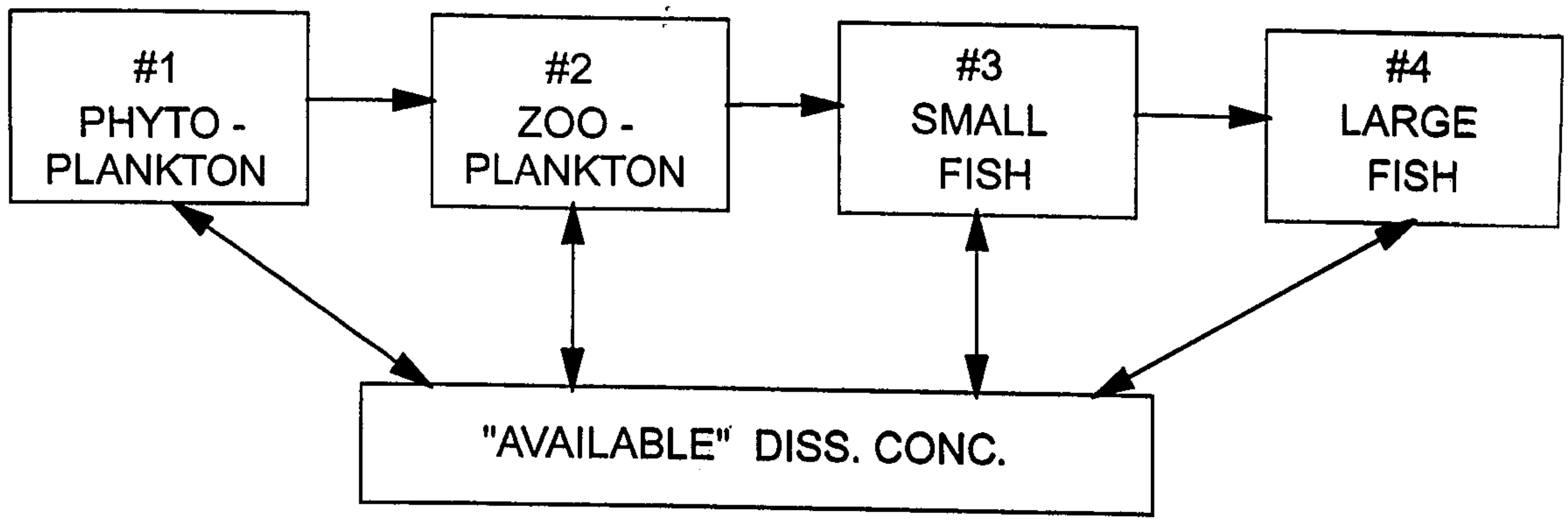
Define a **BIOACCUMULATION FACTOR (BAF)** as ratio fish conc./diss. water conc. where **all routes are included:**

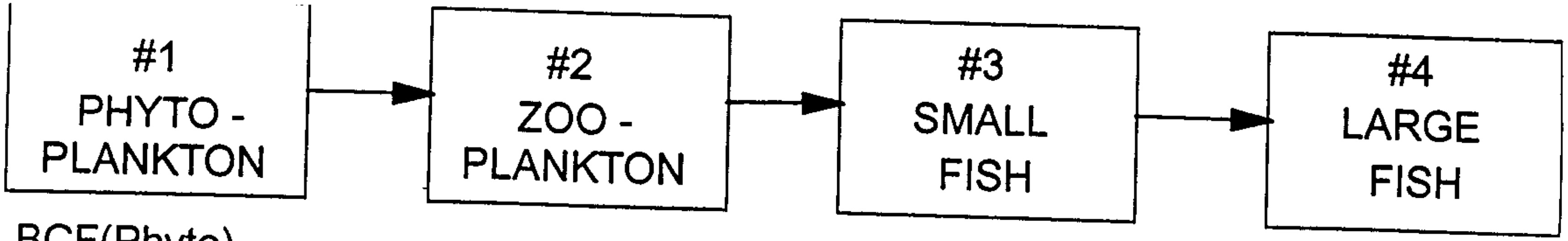
$$BAF(fish) = C(fish)/c(diss) = BCF + g\, BAF(food)$$

NOTE:

1. Accumulation due to food depends on biomagnification ratio: g (a function of chemical assimialtion eff., ingestion rate and loss rate)
2. If g "large"(e.g. >1), food route important. If g "small", (e.g.<<1), food route not important.

A SIMPLE FOUR LEVEL PELAGIC FOOD CHAIN





BCF(Phyto)

BAF(Zoop) = BCF(Zoop) + g(21)BCF(Phyto)

BAF(SmF) = BCF(SmF) + g(32)BAF(Zoop)

BAF(LgF) = BCF(LgF) + g(43)BAF(SmF)

FOR ILLUSTRATION OF CLARITY, SUPPOSE ALL BCF's ARE EQUAL AND ALL BIOMAGNIFICATION RATIOS ARE EQUAL. THEN,

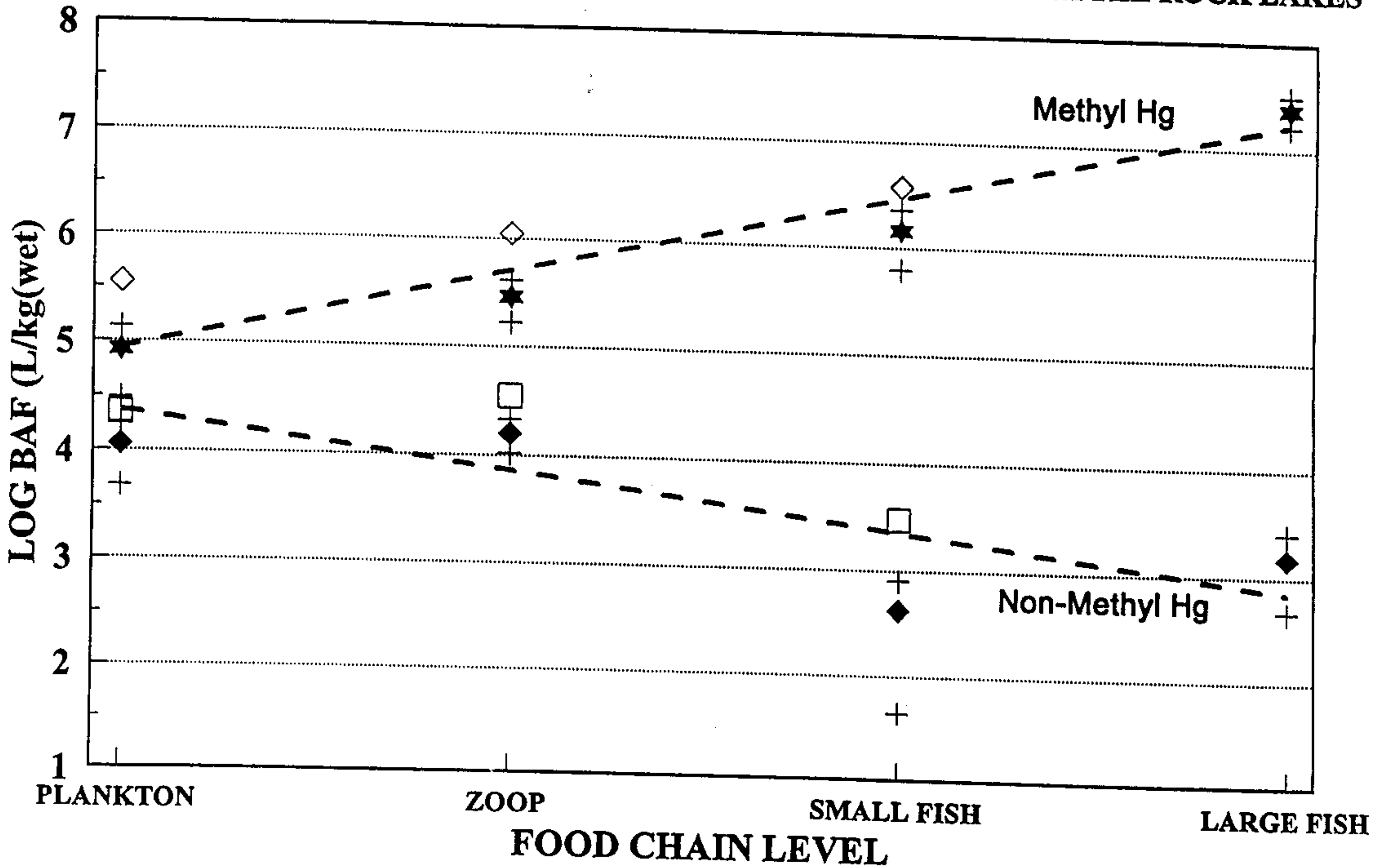
BAF(Zoop) = [1 + g] BCF

BAF(SmF) = [1 + g + g*g] BCF

BAF(LgF) = [1 + g + g*g + g*g*g]BCF

NOTE: FOOD CHAIN BIOACCUMULATION

VARIATION OF MERCURY BAF WITH TROPHIC LEVEL: CLEAR & LITTLE ROCK LAKES



Clear Lk: Suchanek et al, 1993, Star,Diamond +/- StD.
Little Rock Lk: Watras and Bloom, 1992