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SMR.780 - 63

FOURTH AUTUMN COURSE ON MATHEMATICAL ECOLOGY

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"Fate and Effects of Toxic Substances in Surface Waters"

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

Fate & Effects of Toxic Substances in Surface Waters

Uniqueness of Toxic Substances Problem:

1. Impact on public health through
   a. Drinking water supply
   b. Contaminated aquatic foodstuffs (fish & shellfish)
   c. Contaminated food stuffs that use aquatic foodstuffs as feed
2. Impact on aquatic ecosystem through
   a. Acute exposure - mortality
   b. Chronic exposure - reproduction, growth
3. Toxic Substances Problems Not Always Visible
   Acute Public Health Effects vs. Chronic Long Term Effects
4. Some Toxics Bioaccumulate in Food chain
   Lipid Soluble Organic chemicals
   Metals
   Radionuclides
5. Laboratory Analyses - Critical

   Need high level of laboratory competence & quality control

   $\mu g/l$ = ppb } water column
   ng/l = ppt } water column

   $\mu g/g$ = ppm } Sediment / Fish

6. Suspended Solids Important

Toxic may adsorb on to particulate solids

Particulate Toxic $\rightleftharpoons$ Dissolved Toxic

7. Sediment Underneath Water Column May be a "Reservoir" of Toxic

Net Settling ↓ Sediment

↑ Diffusion of Toxic from Sediment

8. Other Pathways

Microbial Biodegradation
Photolysis
Hydrolysis
Volatilization

***** INTRODUCTION *****

WORKING DEFINITION OF A TOXIC SUBSTANCE
A chemical becomes "toxic", in some sense, when it is present in the aquatic environment (either in the water column, sediment, or aquatic organisms) in concentrations so as to cause an interference with a desirable water use.

COMPONENTS OF THE DEFINITION

Exposure Concentration – Fate of Chemical

"Interference" – Effect of Chemical

"Desirable" Water Use –

Risk Assessment ↘ Public Health, Aquatic Ecology, Recreation, Fishing

Risk Management ↗

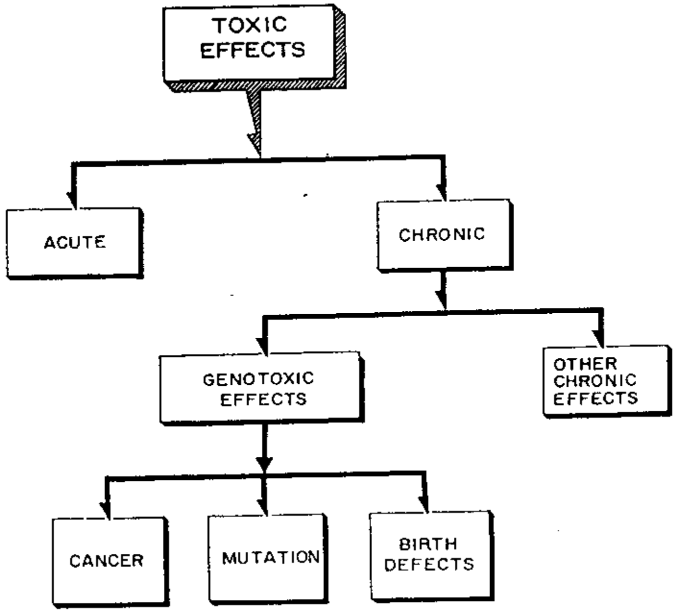
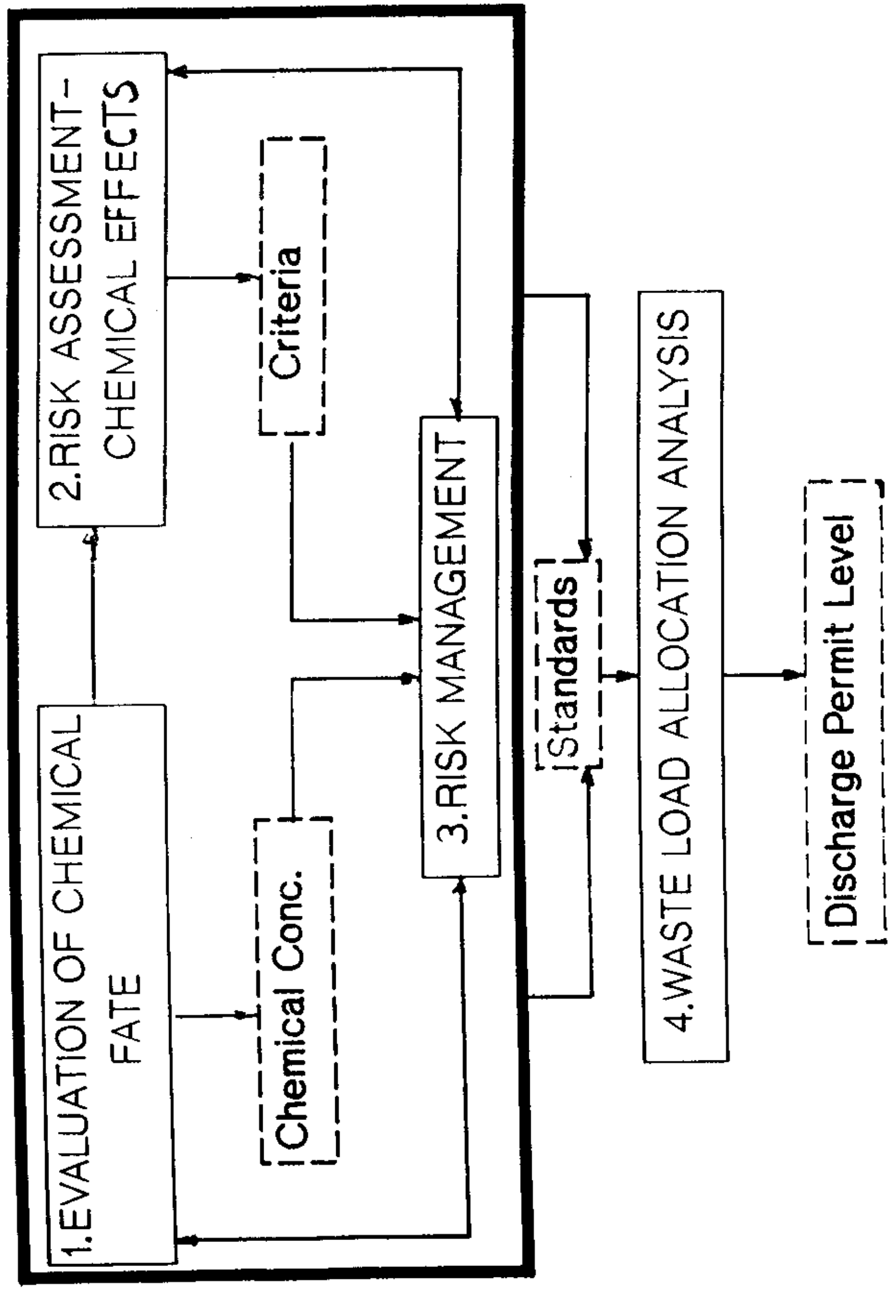


Fig. 2-4 : COMPONENTS OF TOXIC EFFECTS OF CHEMICALS (From USEPA, 1979)



GENERAL PROBLEM IDENTIFICATION FRAMEWORK

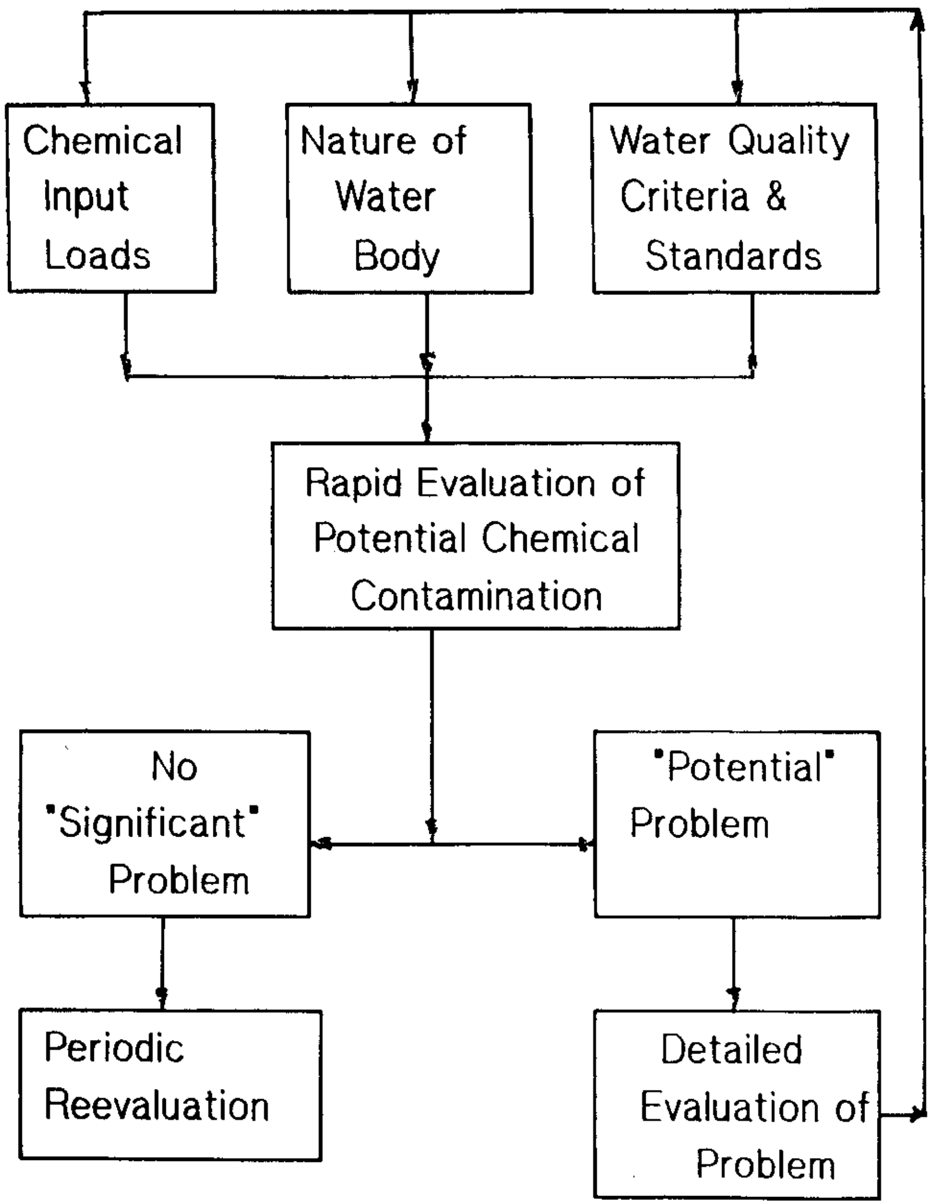


TABLE 3-4

Some Maximum Allowable Concentrations in Fish
("Action Limits")
(U.S. Food and Drug Admin., 1978)

Chemical	Maximum Concentration in Fish (Edible portion), ppm[1]
Aldrin/dieldrin	0.3
DDT and metababolites	5.0
Endrin	0.3
Heptachlor/heptachlor epoxide	0.3
Kepone	0.3
Mercury	1.0
Mirex	0.1
Polychlorinated biphenyls (PCB's)	5.0[2]
Toxaphene	5.0

(1) ppm = one part chemical per million parts wet weight of fish = μg/g(w); g(w) = gm wet weight

(2) 2.0 ppm subsequently adopted by USFDA

Two Complementary Approaches to Analyzing Impact of Chemical Discharges

Chemical Specific Approach	Analyze individual chemicals
Whole Effluent and In-Stream Toxicity Approach	Analyze whole mixture using a toxicity end point

Chemical Specific

Advantages:	Treatability data available Fate can be modeled and predicted Bioaccumulation can be measured and analyzed
Disadvantages:	Which compound is toxic in mixture? Expensive to measure many chemicals Interactions not accounted for.

Toxicity Approach

Advantages:	Aggregate toxicity measured Limit one parameter-toxicity Interactions between chemicals -measured.
Disadvantages:	Treatability data lacking Fate of toxicity not clear Propertics of specific chemicals for public health (bioaccumulation, carcinogenicity) not assessed.

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)

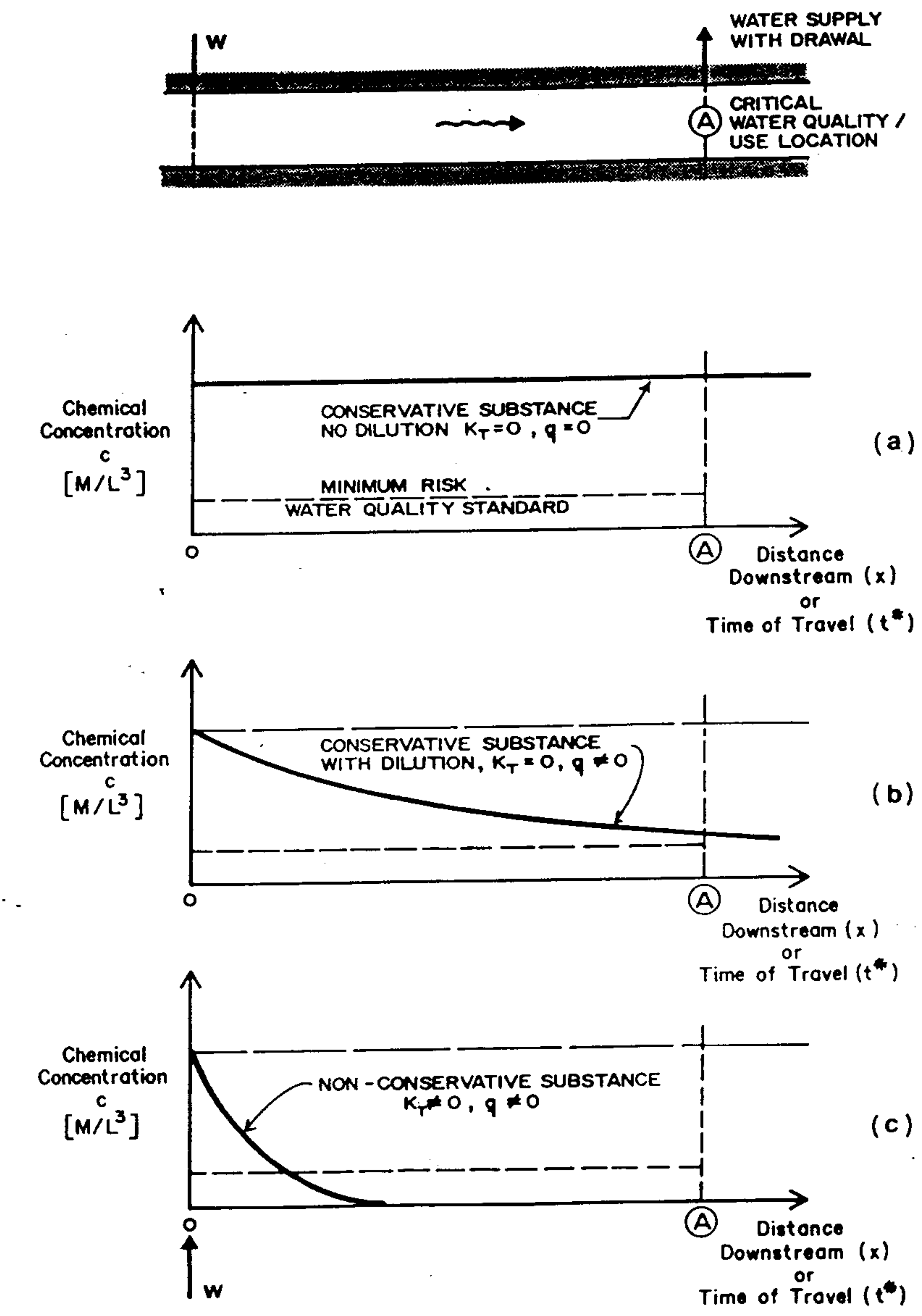
Food Web: In muscle, organs, lipid of fish and other aquatic organisms

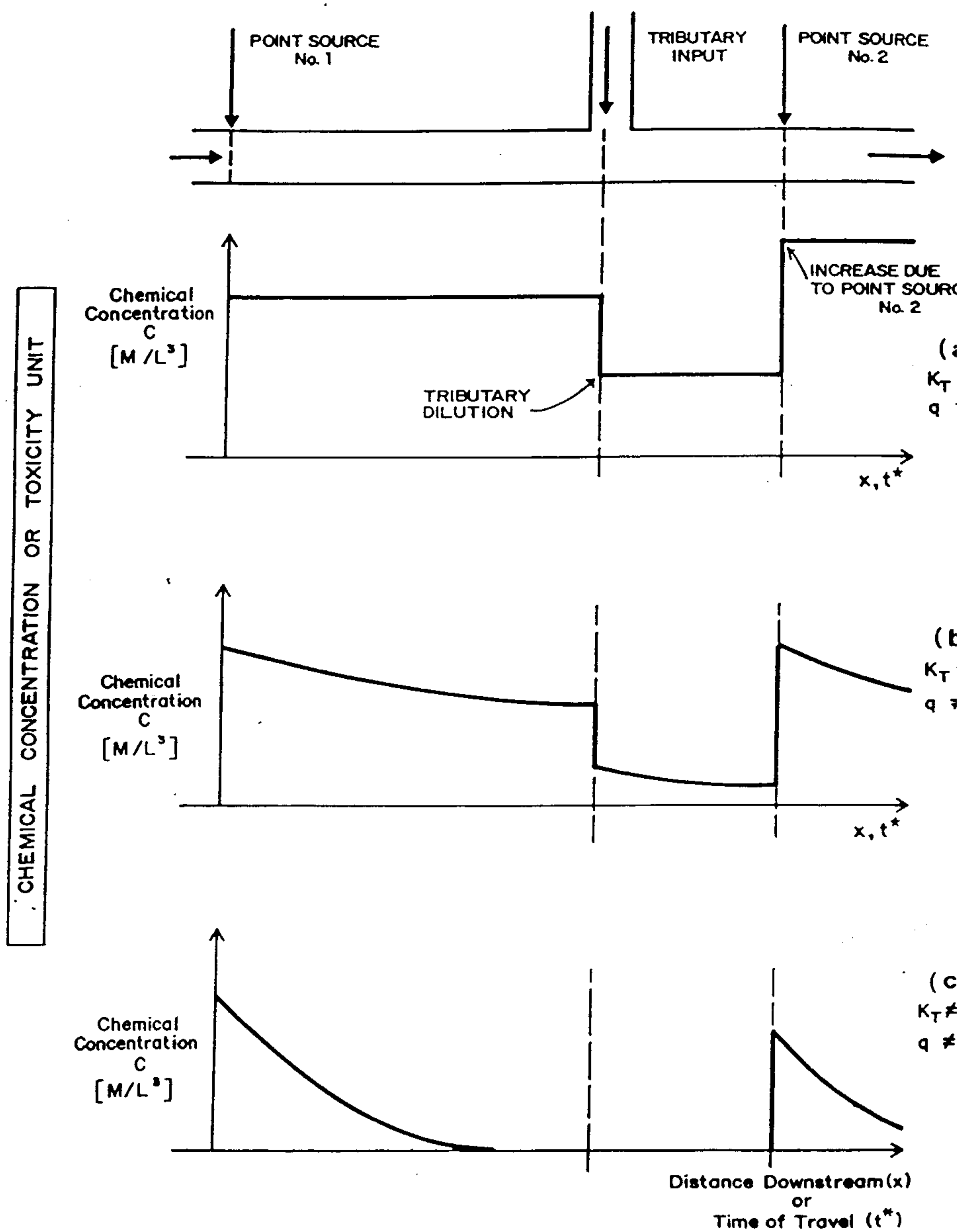
Atmosphere: Gaseous phase
Sorbed to particulates
Dissolved in precipitation

TOXICS ANALYSIS - RIVERS AND STREAMS

A. SIGNIFICANCE OF SUSPENDED SOLIDS
1. DYNAMIC BEHAVIOR
2. DEPOSITIONAL ZONES VARIABLE IN SPACE
3. PERIODS OF NET EROSION
4. SIMPLIFICATIONS POSSIBLE BUT MAY NEED SEDIMENT TRANSPORT MODEL

B. REVIEW OF GENERAL STREAM QUALITY RESPONSE


W
WATER SUPPLY WITH DRAWAL
A CRITICAL WATER QUALITY / USE LOCATION
Chemical Concentration c [M/L3]
CONSERVATIVE SUBSTANCE NO DILUTION KT=0, q=0
MINIMUM RISK WATER QUALITY STANDARD
(a)
0
A
Distance Downstream (x) or Time of Travel (t*)
Chemical Concentration c [M/L3]
CONSERVATIVE SUBSTANCE WITH DILUTION, KT=0, q≠0
(b)
0
A
Distance Downstream (x) or Time of Travel (t*)
Chemical Concentration c [M/L3]
NON-CONSERVATIVE SUBSTANCE KT≠0, q≠0
(c)
0
W
A
Distance Downstream (x) or Time of Travel (t*)


CHEMICAL CONCENTRATION OR TOXICITY UNIT
POINT SOURCE No. 1
TRIBUTARY INPUT
POINT SOURCE No. 2
Chemical Concentration C [M/L³]
INCREASE DUE TO POINT SOUR No. 2
TRIBUTARY DILUTION
x, t*
Distance Downstream (x) or Time of Travel (t*)

C. SUSPENDED SOLIDS EQUATIONS

@ STEADY STATE

WATER COLUMN (with constant flow)

$$0 = -u\,dm_1/dx \;-\; v_s/H_1 m_1 + v_u/H_1 m_2$$

STATIONARY SEDIMENT

$$0 = v_s m_1 - v_u m_2 - v_d m_2$$

FOR A DEPOSITIONAL RIVER ENVIRONMENT AND NO FLOW DILUTION

$$u\,dm_1/dx = -(v_n/H_1)\,m_1(x)$$

WHERE

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

AND THE SOLUTION FOR THIS CASE IS

$$m_1 = m_1(0)\exp(-(v_n/H_1 u)x)$$

FOR CASE WHERE EROSION OCCURS IN DOWNSTREAM DIRECTION[1]:

$$m_1 = m_1(0)\exp(-(v_s/H_1 u)x) + (v_u m_2/v_s)[1 - \exp(-(v_s H_1 u)x)]$$

THE SOLIDS PROFILE THEN BUILDS UP TO AN EQUILIBRIUM VALUE OF SOLIDS GIVEN BY

$$m_1(\infty) = v_u m_2/v_s$$

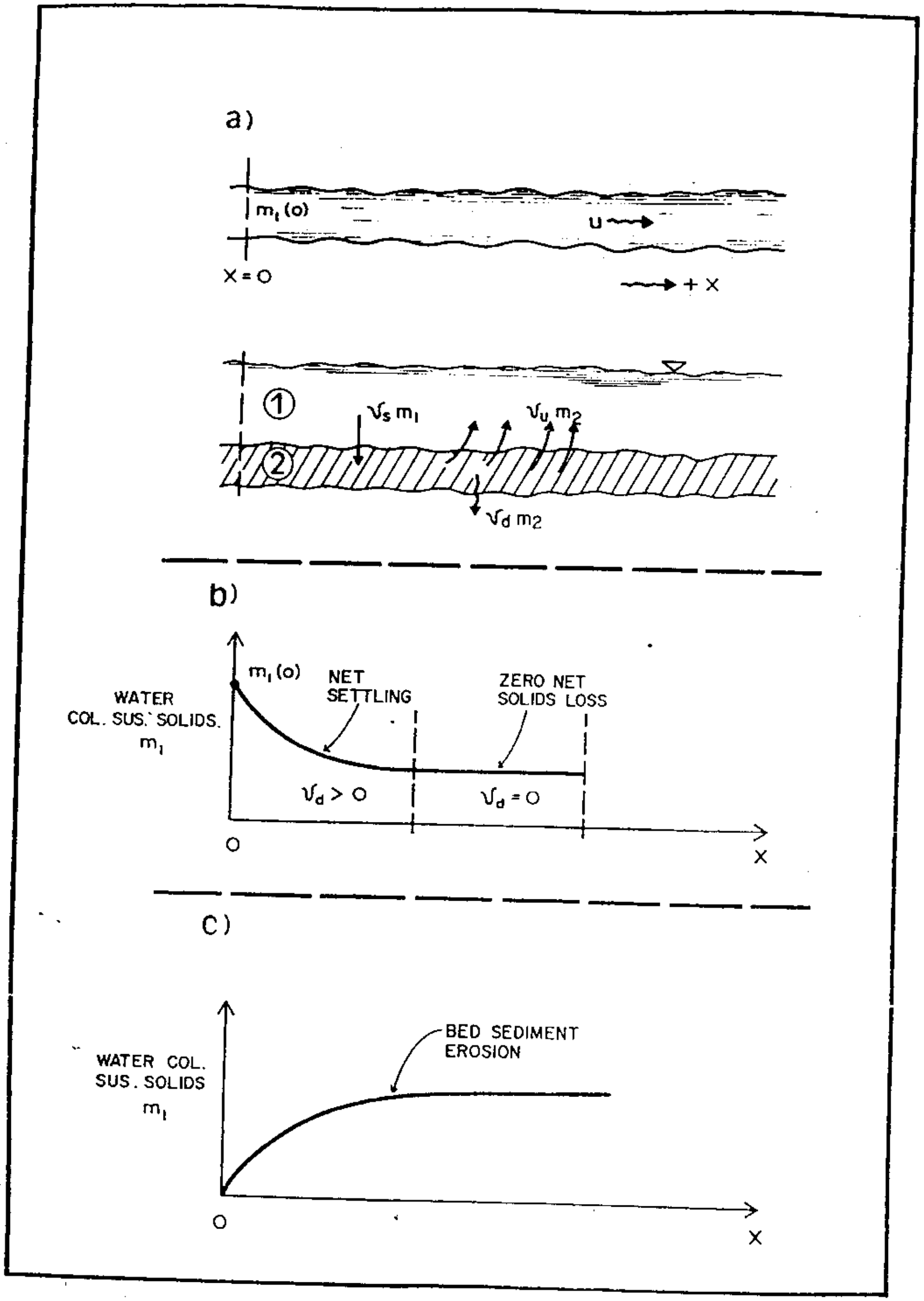
For the equilibrium solids estimated from the profile and m_2 and v_s known, the resuspension velocity can be estimated.

Also can show from above eqs:

$$\frac{m_1}{m_1(0)} = \phi + (1-\phi)e^{-((v_s/H_1 u)x)}$$

where $\phi = \dfrac{\text{entrainment flux of solids}}{\text{settling flux of solids}} = \dfrac{v_u m_2}{v_s m_1}$

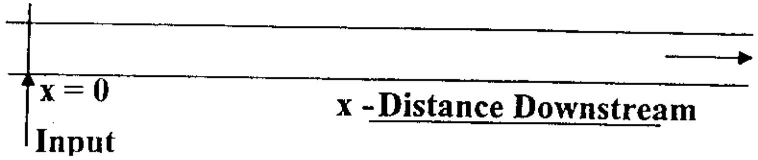
1 O'Connor, D.J., 1988. Models of sorptive toxic substances in freshwater systems. I: Basic equations. ASCE, J.Env. Eng. Div., 114(3):507 - 532.



D. TOXICS MODEL - RIVERS AND STREAMS
PROCESSES:

SEDIMENT DIFFUSIVE EXCHANGE
AIR - WATER EXCHANGE
LOSS OF CHEMICAL FROM SYSTEM
SETTLING FLUX OF CHEMICAL
RESUSPENSION FLUX OF CHEMICAL
NET BURIAL OF CHEMICAL

STEADY STATE MASS BALANCE EQUATIONS:



WATER COLUMN

$udc_{T1}/dx = K_f/H_1(f_{d2}c_{T2}/\phi_2 - f_{d1}c_{T1})$	Sediment diffusive exchange
$-K_{T1}c_{T1}$	Loss (photolysis,biodegrad.)
$+k_l/H_1(c_g/H_e - f_{d1}c_{T1})$	Air/water exchange
$-v_s/H_1(f_{p1}c_{T1})$	Settling
$+v_u/H_1(f_{p2}c_{T2})$	Resuspension

STATIONARY SEDIMENT

$0 = - K_f/H_1(f_{d2}c_{T2}/\phi_2 - f_{d1}c_{T1})$	Sediment diffusive exchange
$-K_{T2}c_{T2}$	Loss (photolysis,biodegrad.)
$+v_s/H_2(f_{p1}c_{T1})$	Settling
$-v_u/H_2(f_{p2}c_{T2})$	Resuspension
$-v_d/H_2(f_{p2}c_{T2})$	Net Deposition

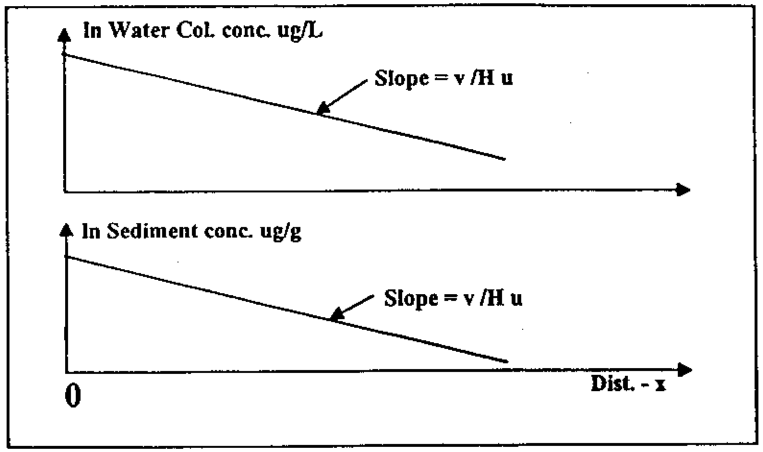
SOLUTION:

Total concentration in Water Column
$c_{T1} = (W_T/Q) \exp[-(v_T/H_1)(x/u)]$

Sediment Particulate Concentration
$r_2 = (\delta f_{p1}/m_1)\, c_{T1}(x)$

$= (\delta f_{p1}/m_1)\, (W_T/Q) \exp[-(v_T/H_1)(x/u)]$

Note: The shape of the profile in the downstream direction is the same for the water column concentration and the sediment particulate concentration.

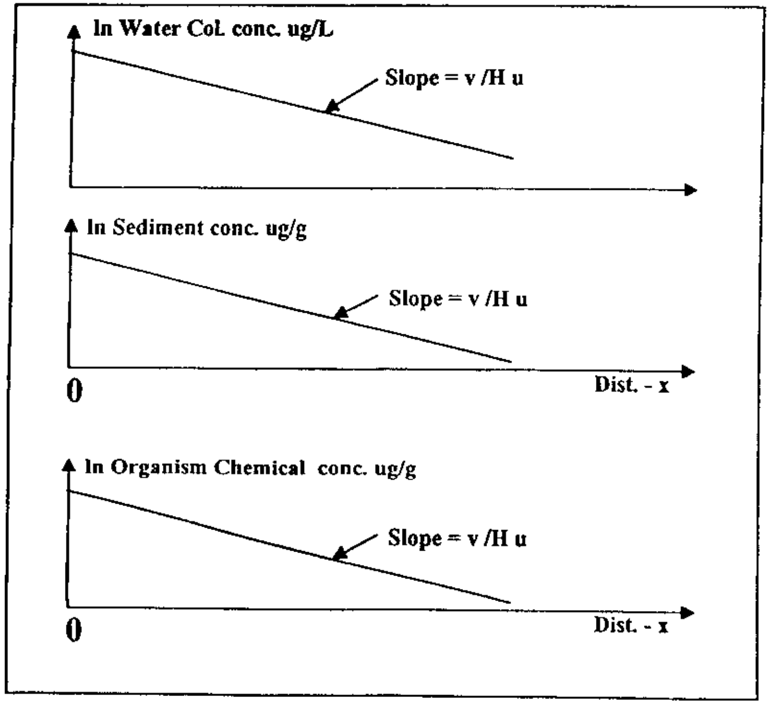


THEREFORE, THE CHEMICAL CONCENTRATION IN THE ORGANISM IS

$$\nu = N c_{d1}$$

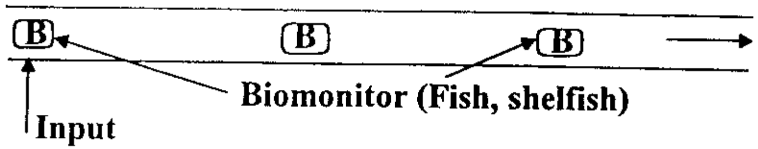
$$= N\ f_{d1}\ (W_T/Q)\ \exp[-(v_T/H_1)(x/u)]$$

AGAIN, THE DOWNSTREAM PROFILE FOR THE ORGANISM CHEMICAL CONCENTRATION IS THE SAME AS FOR THE WATER COLUMN AND SEDIMENT.



RELATIONSHIP OF AQUATIC ORGANISM CONCENTRATION TO DISSOLVED CHEMICAL CONCENTRATION IN RIVERS

ASSUME: ORGANISM DOES NOT MIGRATE SIGNIFICANT DISTANCE IN RIVER OR ORGANISM IS IN CAGE POSITIONED AT VARIOUS LOCATIONS DOWNSTREAM



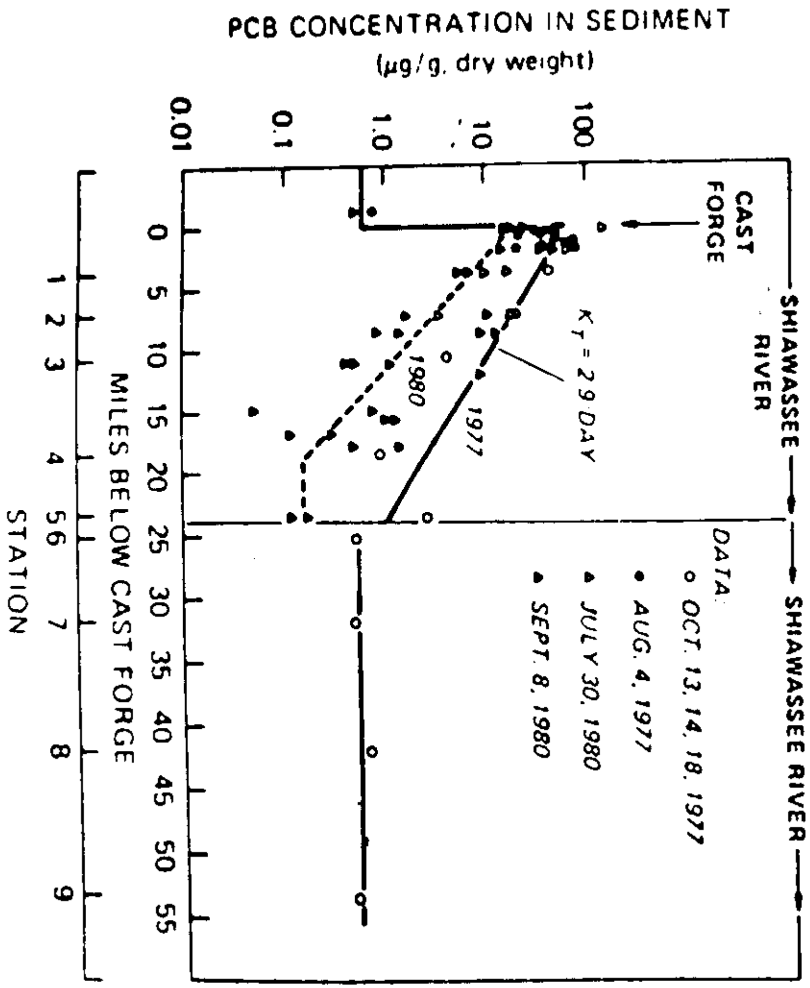
DEFINE ν = chemical concentration in organism (ug/g(wet))

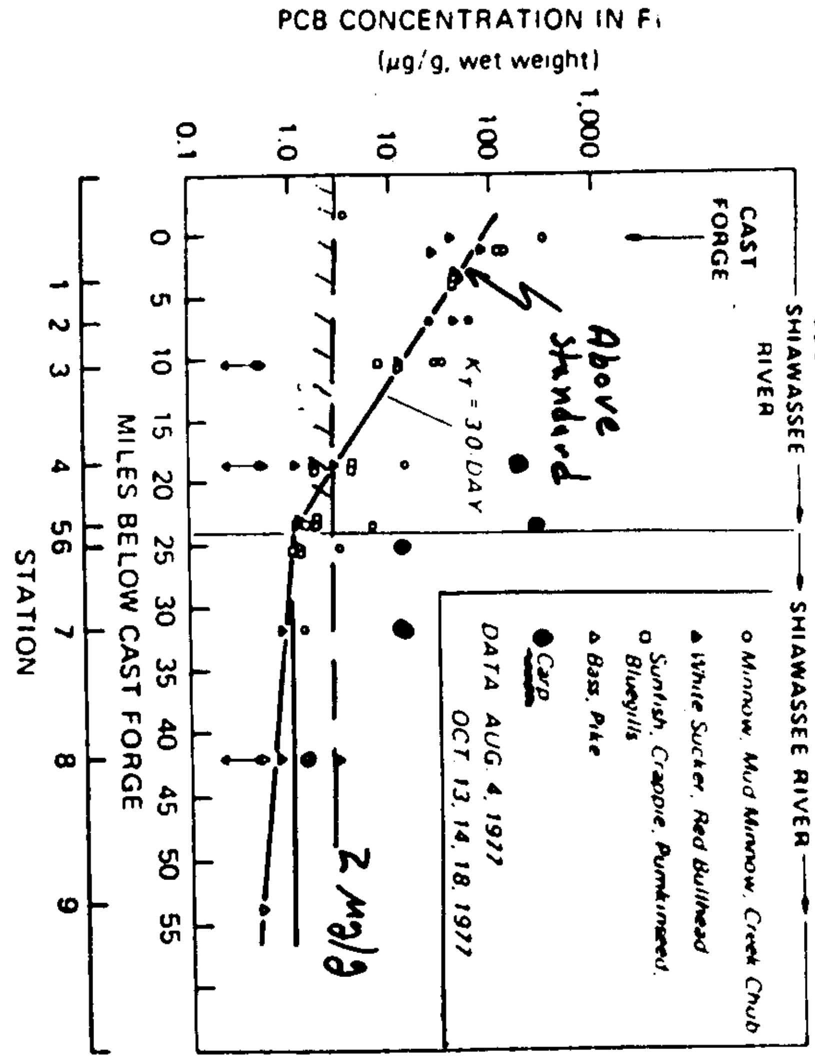
N = Bioaccumulation Factor (BAF)

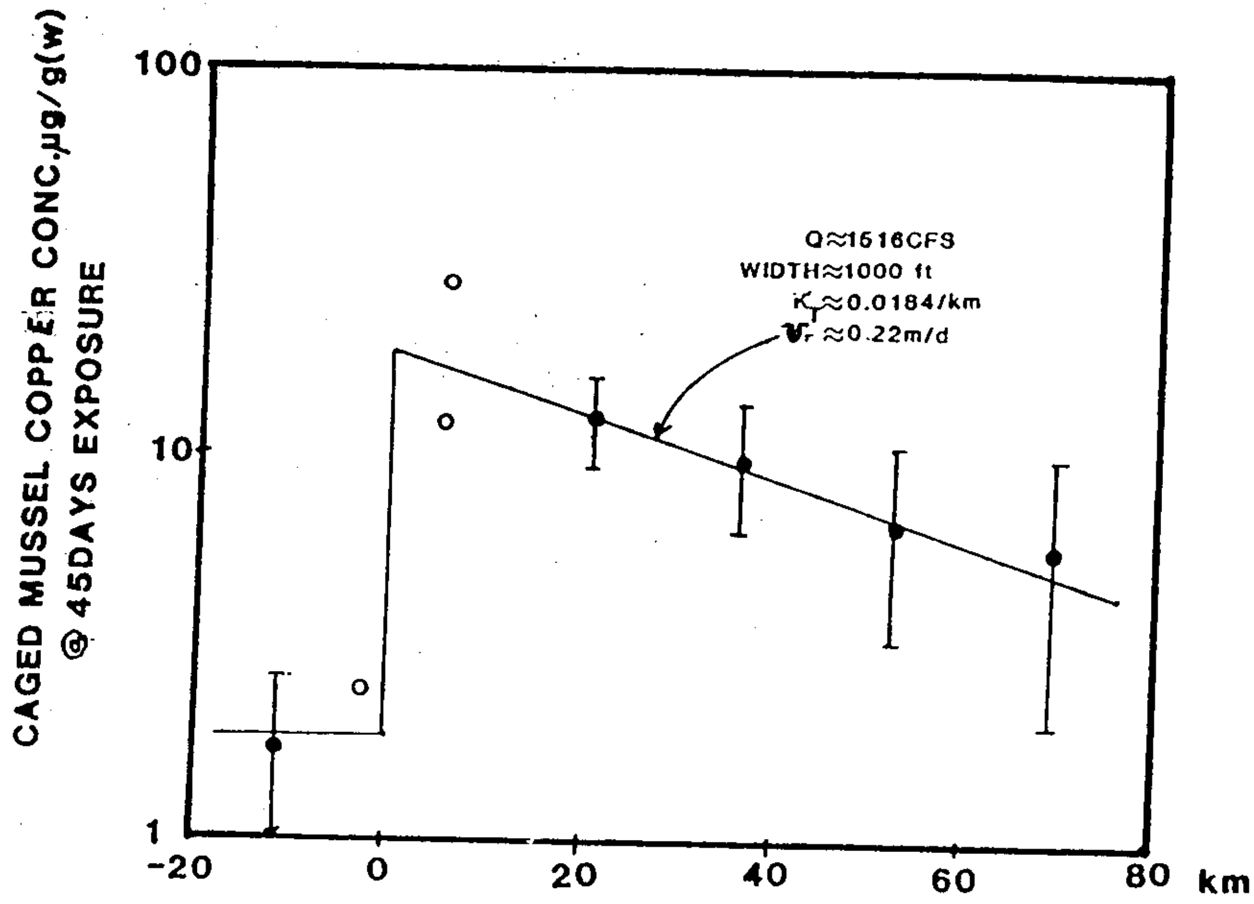
= ν/c_d = ratio of chemical in organism to dissolved chemical in water

DISSOLVED CHEMICAL IS GIVEN FROM PREVIOUS SOLUTION FOR TOTAL CHEMICAL, i.e.,

$$c_{d1} = f_{d1}\ c_{T1}(x)$$


PCB CONCENTRATION IN SEDIMENT
(µg/g, dry weight)
0.01
0.1
1.0
10
100
CAST FORGE
SOUTH BR. SHIAWASSEE RIVER
SHIAWASSEE RIVER
K_T = 29 DAY
1980
1977
DATA:
OCT. 13, 14, 18, 1977
AUG. 4, 1977
JULY 30, 1980
SEPT. 8, 1980
0 5 10 15 20 25 30 35 40 45 50 55
MILES BELOW CAST FORGE
1 2 3 4 5 6 7 8 9
STATION


PCB CONCENTRATION IN F
(µg/g, wet weight)
0.1
1.0
10
100
1,000
CAST FORGE
SOUTH BR SHIAWASSEE RIVER
SHIAWASSEE RIVER
K_T = 30 DAY
Above Standard
2 Mg/g
Minnow, Mud Minnow, Creek Chub
White Sucker, Red Bullhead
Sunfish, Crappie, Pumkinseed, Bluegills
Bass, Pike
Carp
DATA AUG. 4, 1977
OCT. 13, 14, 18, 1977
0 5 10 15 20 25 30 35 40 45 50 55
MILES BELOW CAST FORGE
1 2 3 4 5 6 7 8 9
STATION



Variation of Copper Concentration in Caged Mussels, Quadrula quadrula, Muskingum R. Sept 1973, Data from Foster and Bates (1978)

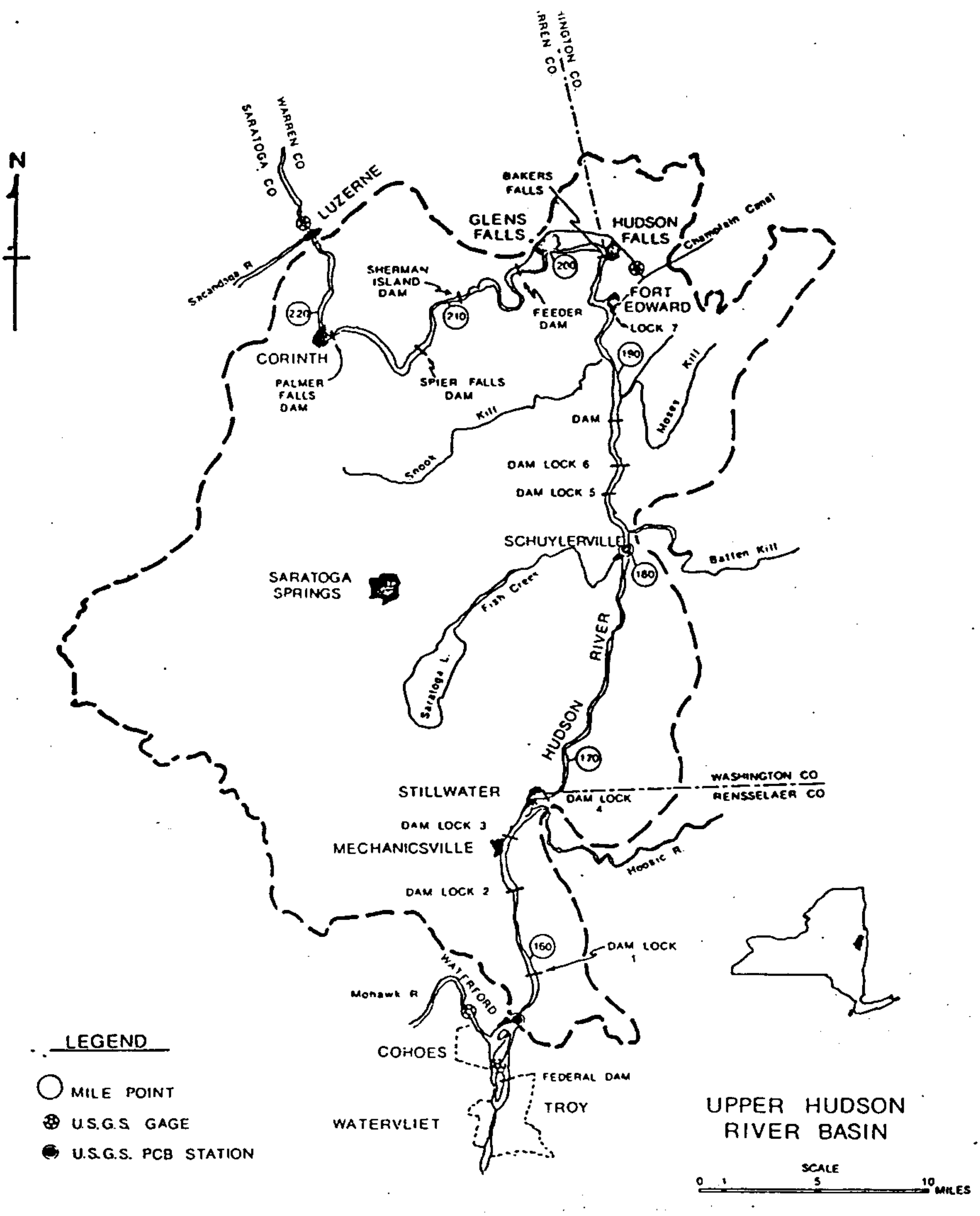


Figure 1. Map of Upper Hudson River PCBs Superfund sites (from NYS DEC).

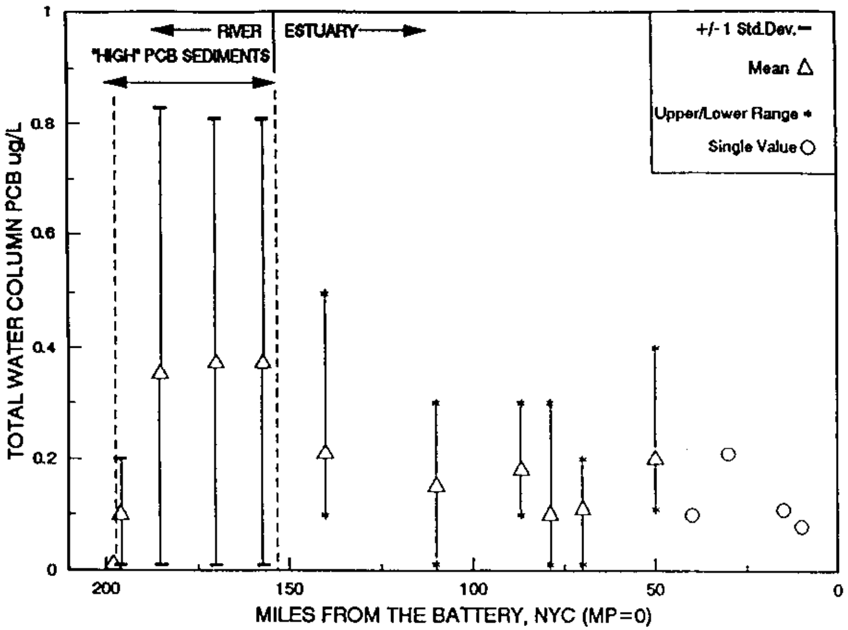


Figure 2. Spatial distribution of water column PCB concentration of Hudson River and Estuary (upper River, 1977-1983, estuary, 1977-1979) Compiled from data of USGS, Poughkeepsie intake, NYC 208 study.

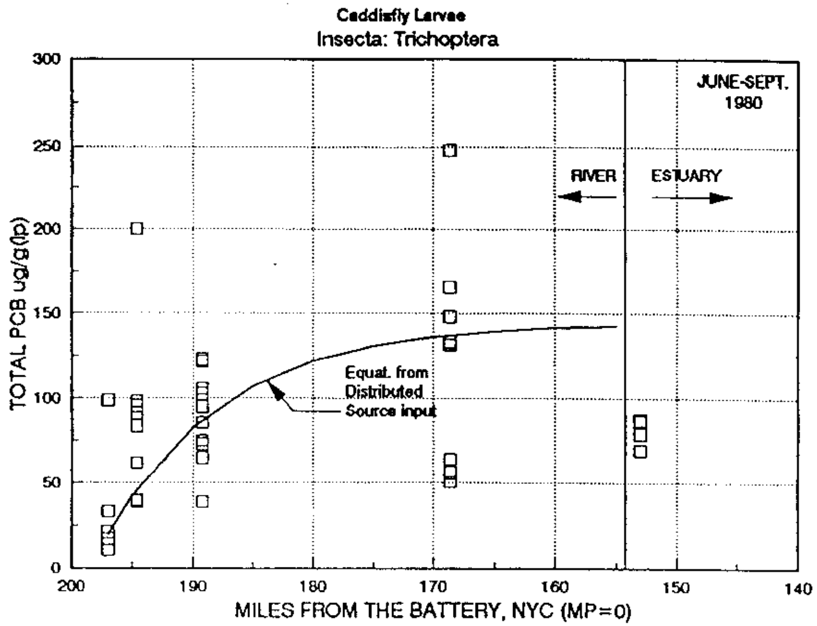


Figure 12. Longitudinal distribution of caddisfly larvae total PCB concentration in site region. Data from NYS DEC. Line is equation resulting from a distributed sediment source of PCB.