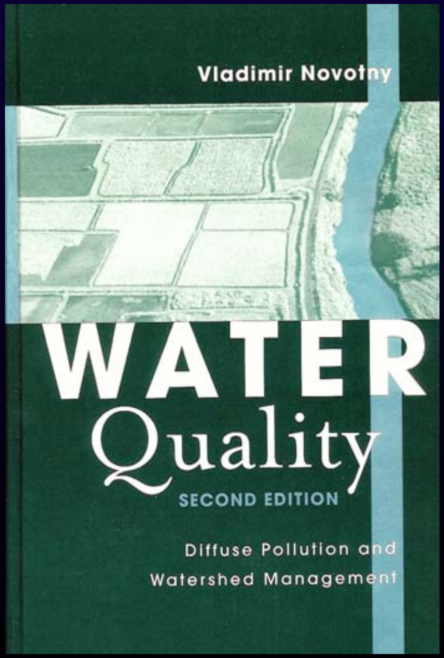
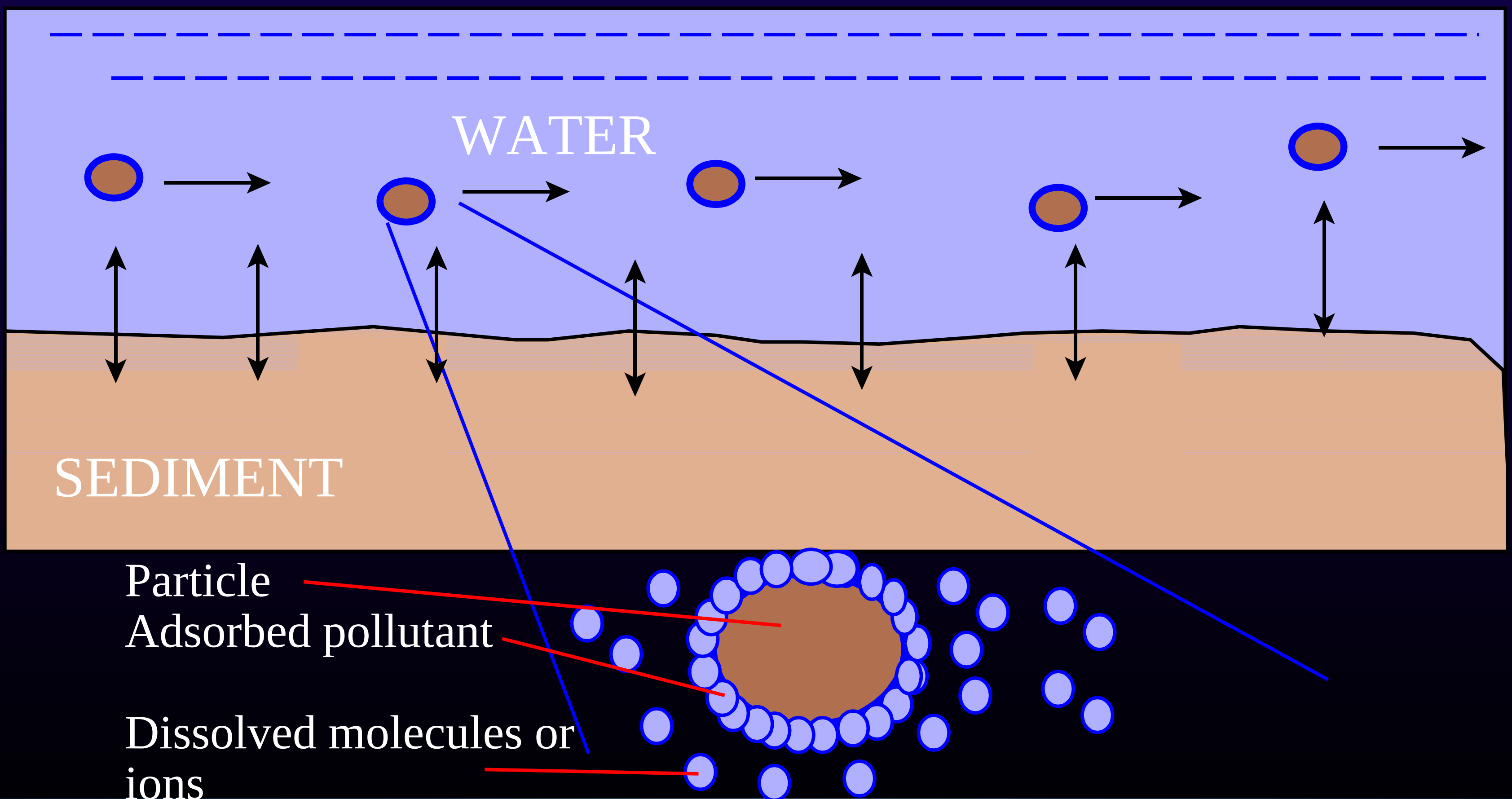
MODELING TOXIC COMPOUNDS



Supplement to Chapter 13

TWO PHASE MOVEMENT OF TOXIC COMPOUNDS



PARTITIONING CONCEPT

Pollutants (hydrophobic organic toxic compounds, ammonium, phosphorus, toxic metals) exist in water or in sediment as

DISSOLVED ⇌ ADSORBED
Ionic form ⇌ Precipitated

Equilibrium

Pb^{++}, Cu^{++} ⇌ CuS, PbS

In particulate form most of the contaminant are not toxic. The dissolved (ionic form) is toxic to aquatic organisms

The adsorption equilibrium is affected by a number of ligants such as pH, organic particulate matter, redox potential (O_2 concentration), clay content, chlorides (salinity), etc.

The adsorption equilibrium between dissolved (ionic) and adsorbed (particulate) forms is expressed by adsorption isotherms , e.g,

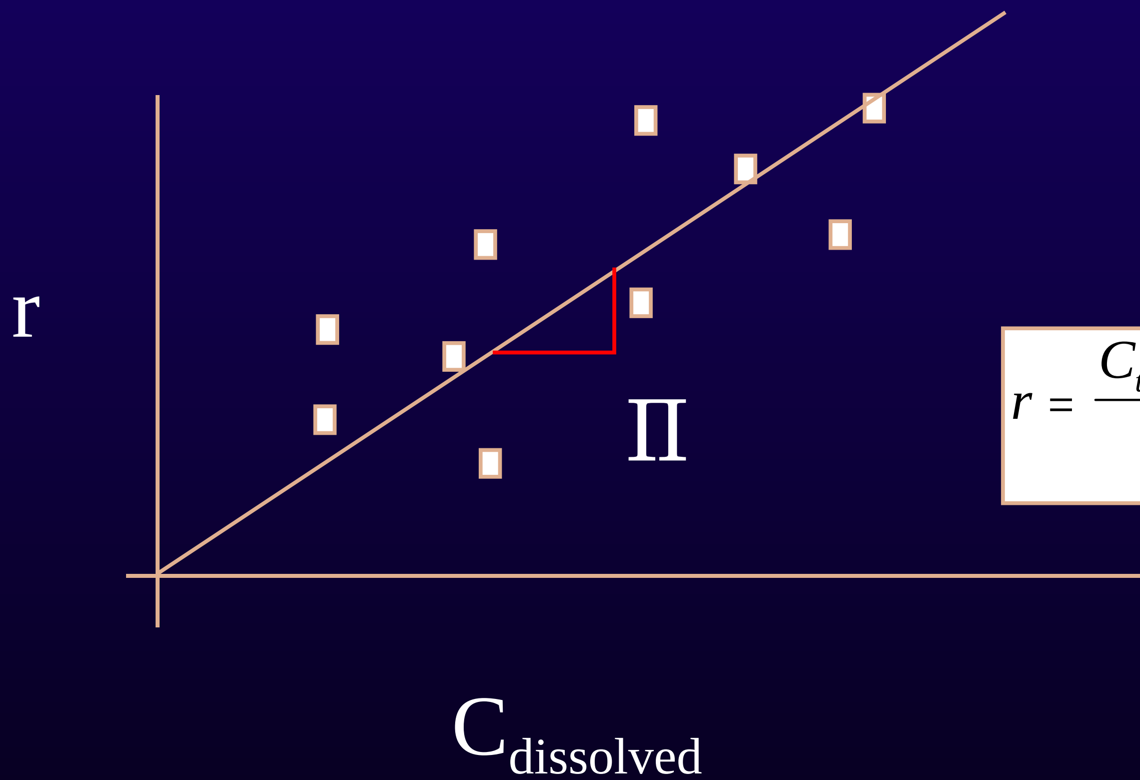
Langmuir

$$r = \frac{Q^0 b C_e}{1 + b C_e}$$

Linear

$$r = \Pi\, C_e$$

r = adsorbed concentration of the contaminant (μg/g of sediment)
C_e = dissolved (ionized) concentration of the contaminant (μg/L)
Q^0= adsorption maximum at fixed temperature (μg/g of sediment)
b= a constant related to energy of the net enthalpy of adsorption (L/μg)
Π= linear partitioning coefficient (L/g)



$$r = \frac{C_{total} - C_{dissoved}}{m_{ss}}$$

Linear Adsorption Isotherm

m_{ss}= concentration of suspended solids or particulate carbon (g/L)

Total pollutant concentration in water

$$C_{total} = C_d + C_p = C_d + m_{ss} r = C_d\,(1 + \Pi\, m_{ss})$$

In water

$$C_e = \frac{C_{total}}{1 + \Pi\, m_{ss}}$$

In sediment

$$C_e = \frac{C_{total}}{\theta + \Pi\, m_{ss}}$$

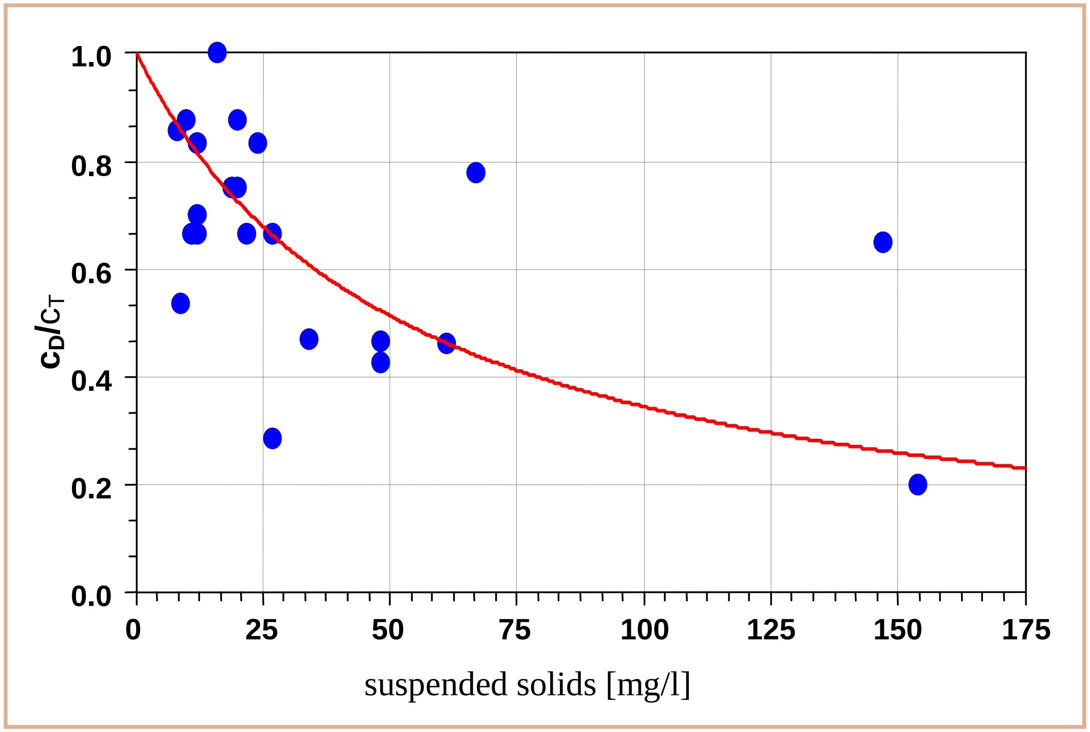
θ = porosity

PARTITIONING

Magnitude of the partitioning coefficient ranges from
1 L/g to 10^6 L/g

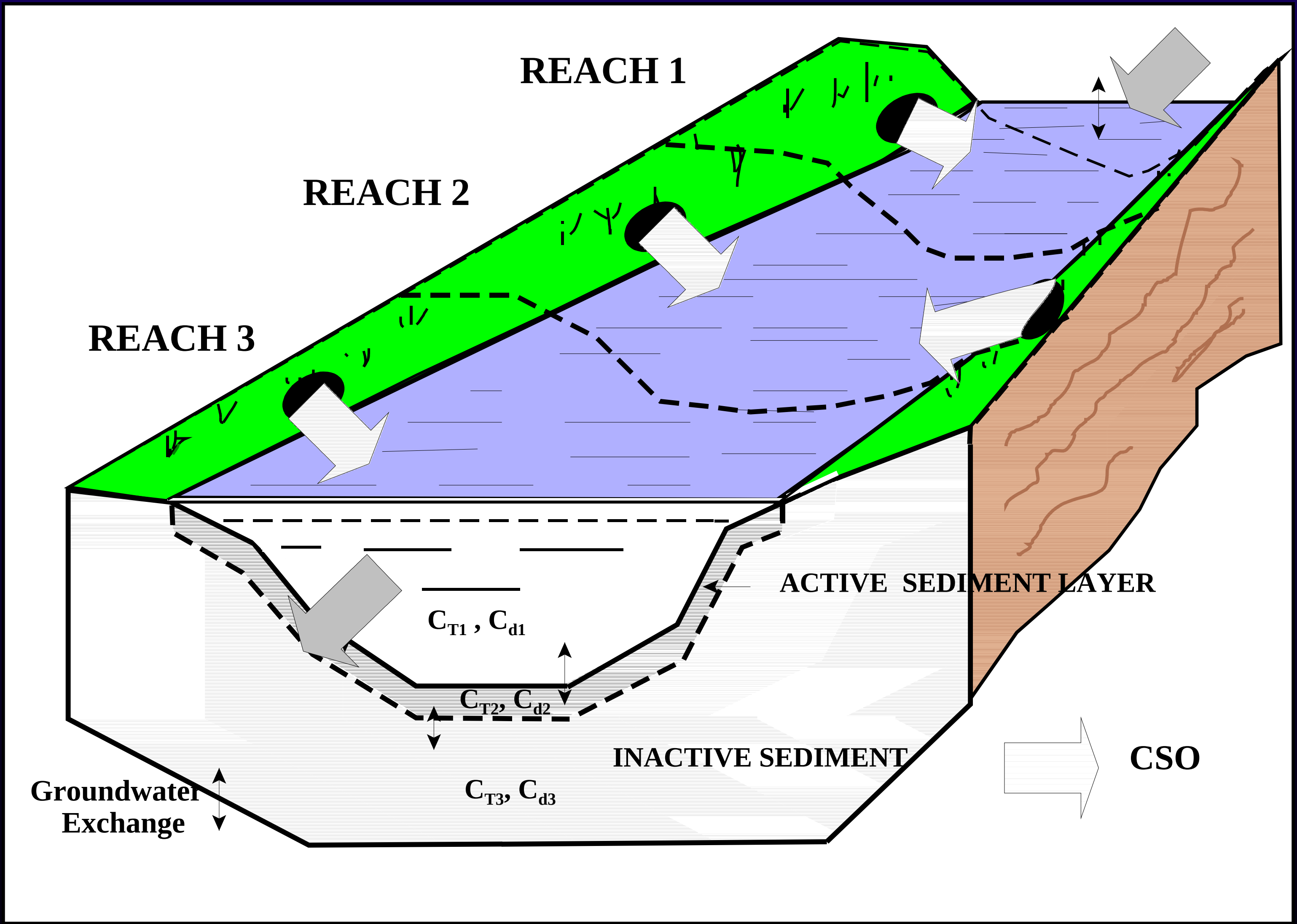
Solvents

PCBs, DDT



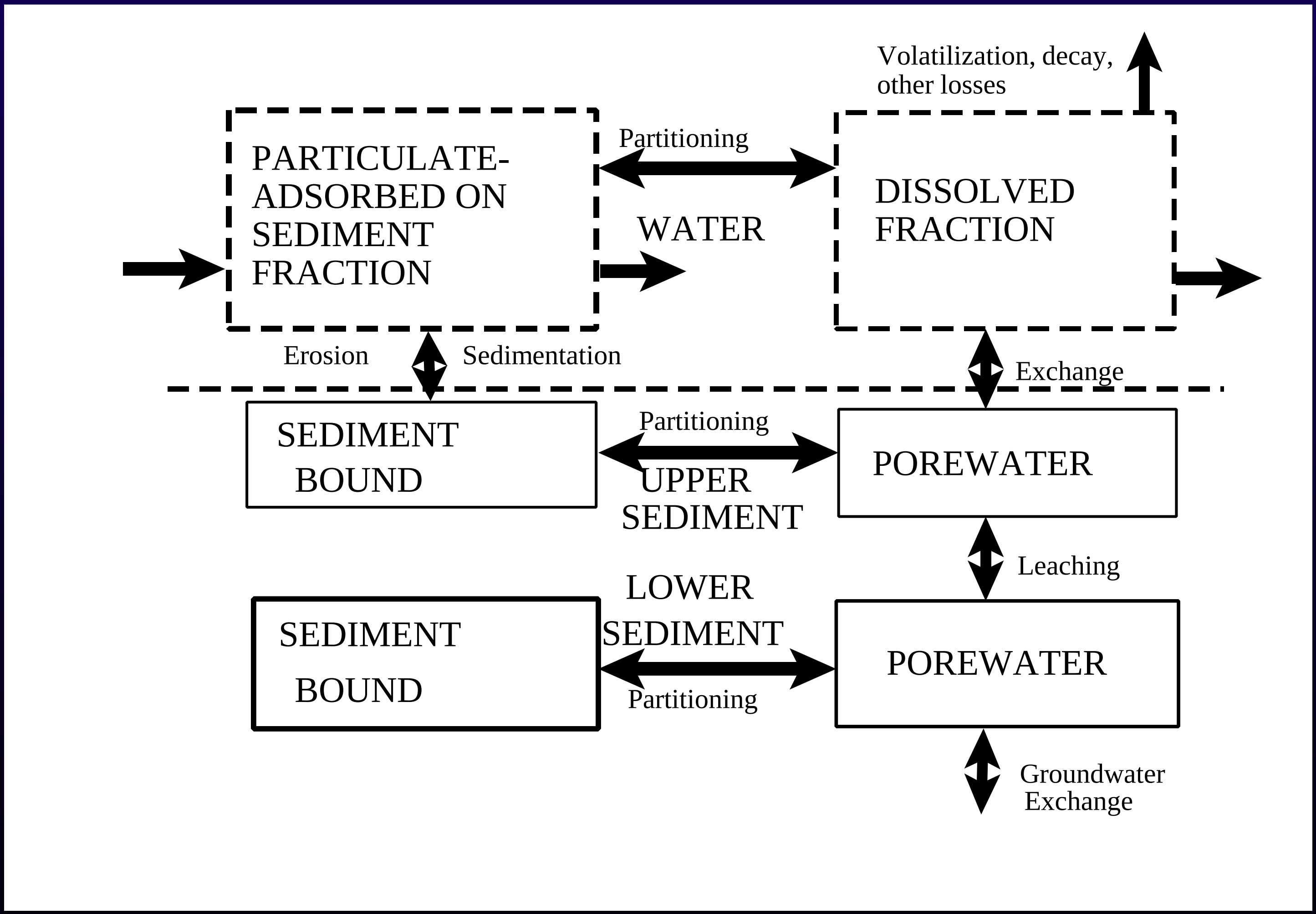
For toxic organics Π is related to the octanol partitioning coefficient K_{ow}

North
Avenue Dam
in Milwaukee



SCHEMATIC OF THE TOXIC MODEL

SCHEMATIC OF THREE LAYER MODEL



TWO PHASE TOXIC COMPOUND TRANSFER

IN WATER

Dissolved

$$\frac{dC_d}{dt} = \frac{W_d}{V} - \frac{C_d}{t_0} - (K_1 + K_c + K_a)C_d + K_2 C_p$$

Particulate

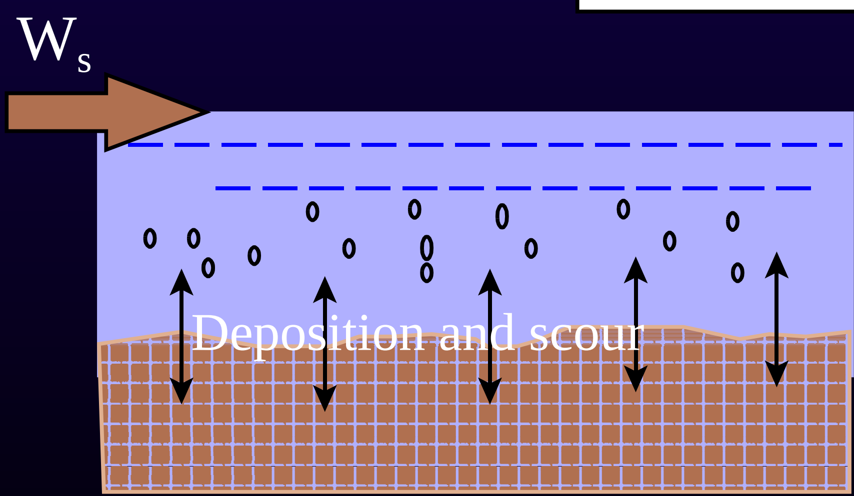
$$\frac{dC_p}{dt} = \frac{W_p}{V} - \frac{C_p}{t_0} + K_1 C_d - (K_2 + K_p + K_s)C_p$$

C_d=dissolved concentration;
V= volume of the computational segment
t_0=detention time within the segment, V/Q
K_2= desorption rate coefficient
K_d =transfer (volatilization) rate coeff.
K_s=v_s/H=sediment transfer rate
v_s=settling (resuspension) velocity

C_p=adsorbed fraction concentration
Q=flow through the segment
K_1=adsorption rate coefficient
K_c= decay rate coefficient,dissolved
K_p=decay rate coeff., particular
W_c, W_p = mass input of the dissolved and adsorbed fractions

SEDIMENT MASS BALANCE

$$\frac{dm}{dt} = \frac{m_i}{t_0} - m\left[\frac{1}{t_0} + K_s\right]$$



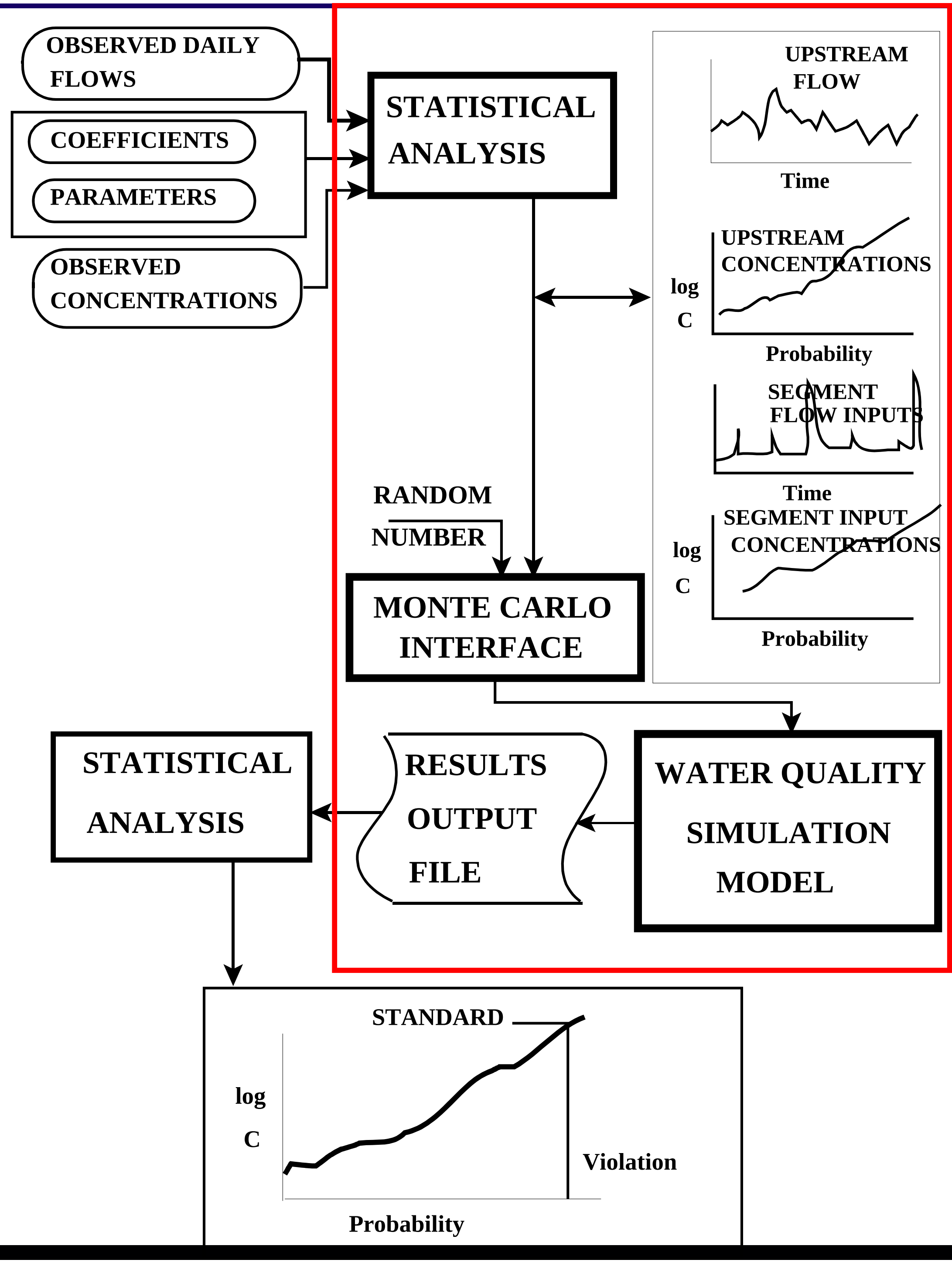
m= concentration of suspended sediment

$m_i = W_s/Q$=average concentration of suspended sediment in the input

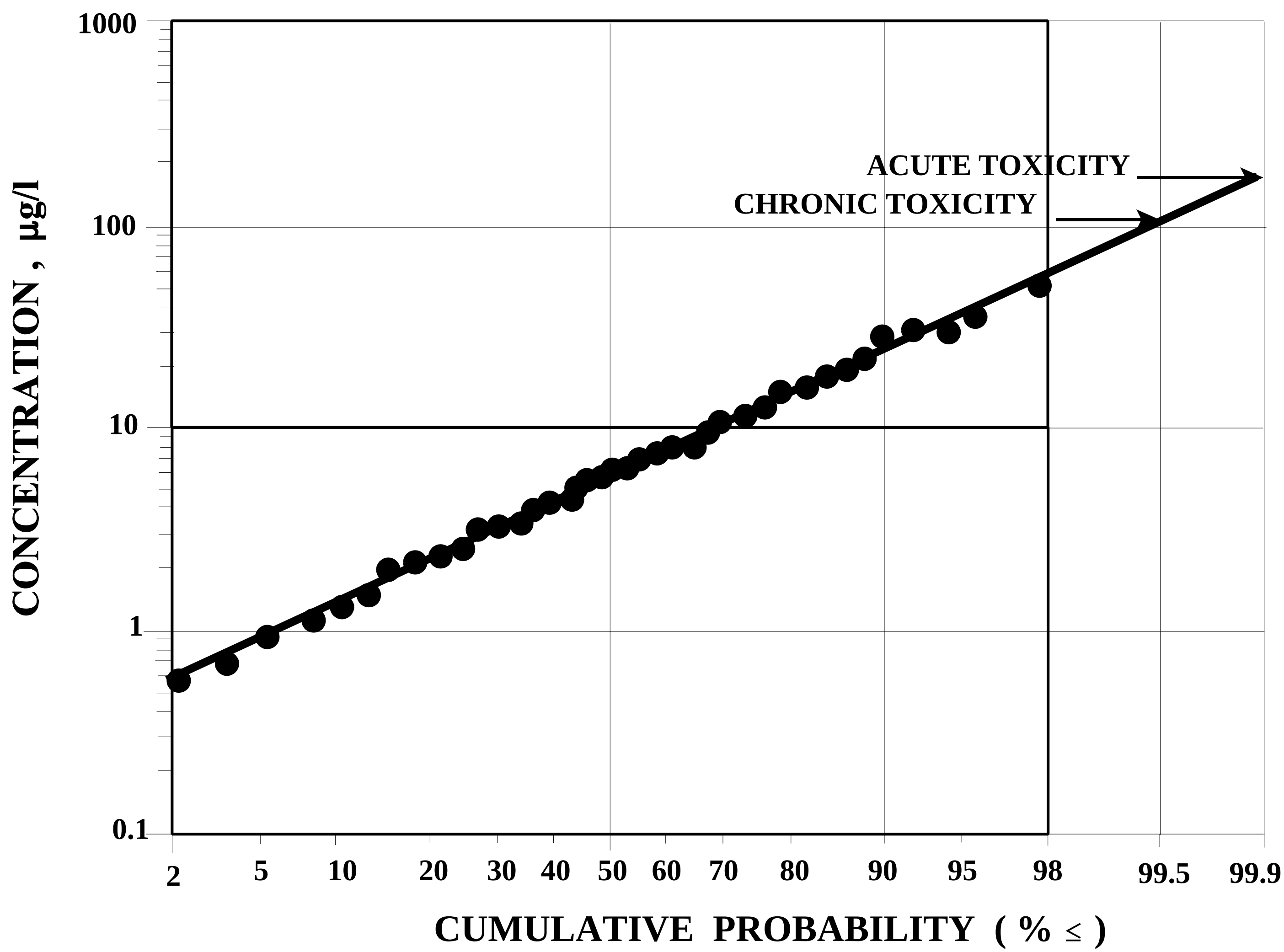
W_s= mass input of suspended solids into the segment

t_0 = residence time in the control volume

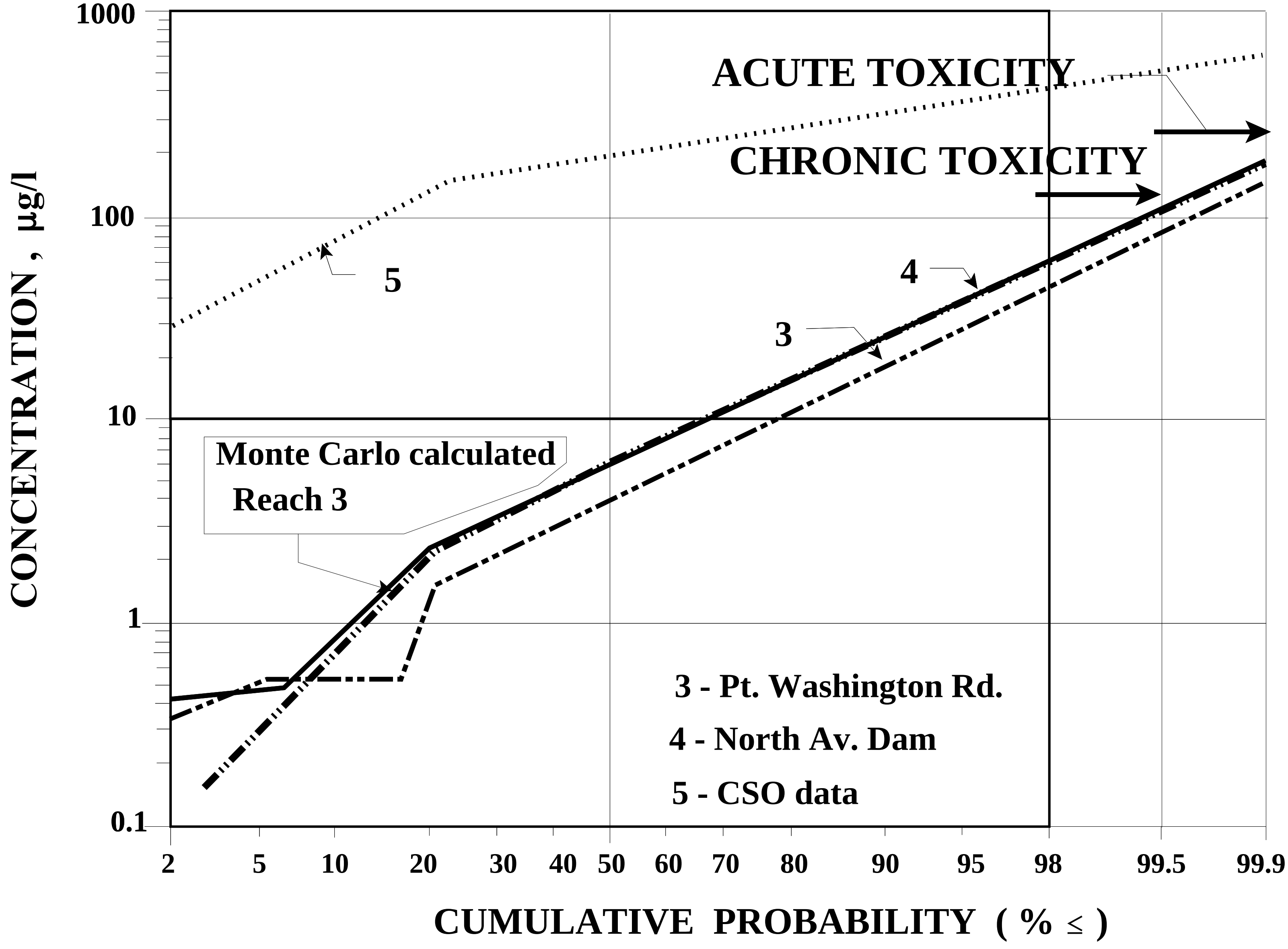
K_s = settling velocity or scour rate



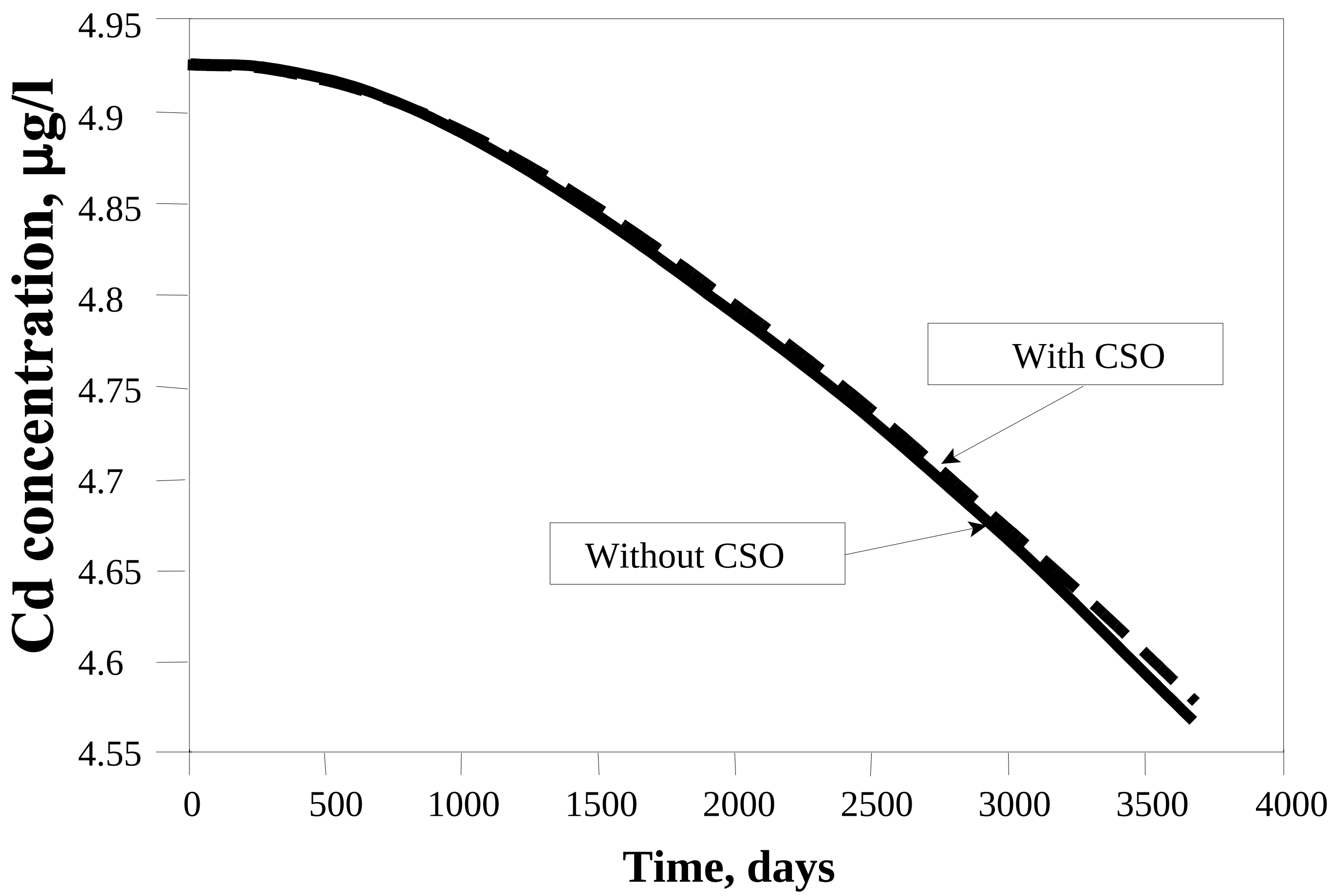
OBSERVED DAILY FLOWS
COEFFICIENTS
PARAMETERS
OBSERVED CONCENTRATIONS
STATISTICAL ANALYSIS
UPSTREAM FLOW
Time
UPSTREAM CONCENTRATIONS
log C
Probability
SEGMENT FLOW INPUTS
Time
SEGMENT INPUT CONCENTRATIONS
log C
Probability
RANDOM NUMBER
MONTE CARLO INTERFACE
STATISTICAL ANALYSIS
RESULTS OUTPUT FILE
WATER QUALITY SIMULATION MODEL
STANDARD
log C
Violation
Probability



1000
100
10
1
0.1
CONCENTRATION , µg/l
ACUTE TOXICITY
CHRONIC TOXICITY
2
5
10
20
30
40
50
60
70
80
90
95
98
99.5
99.9
CUMULATIVE PROBABILITY (% ≤)

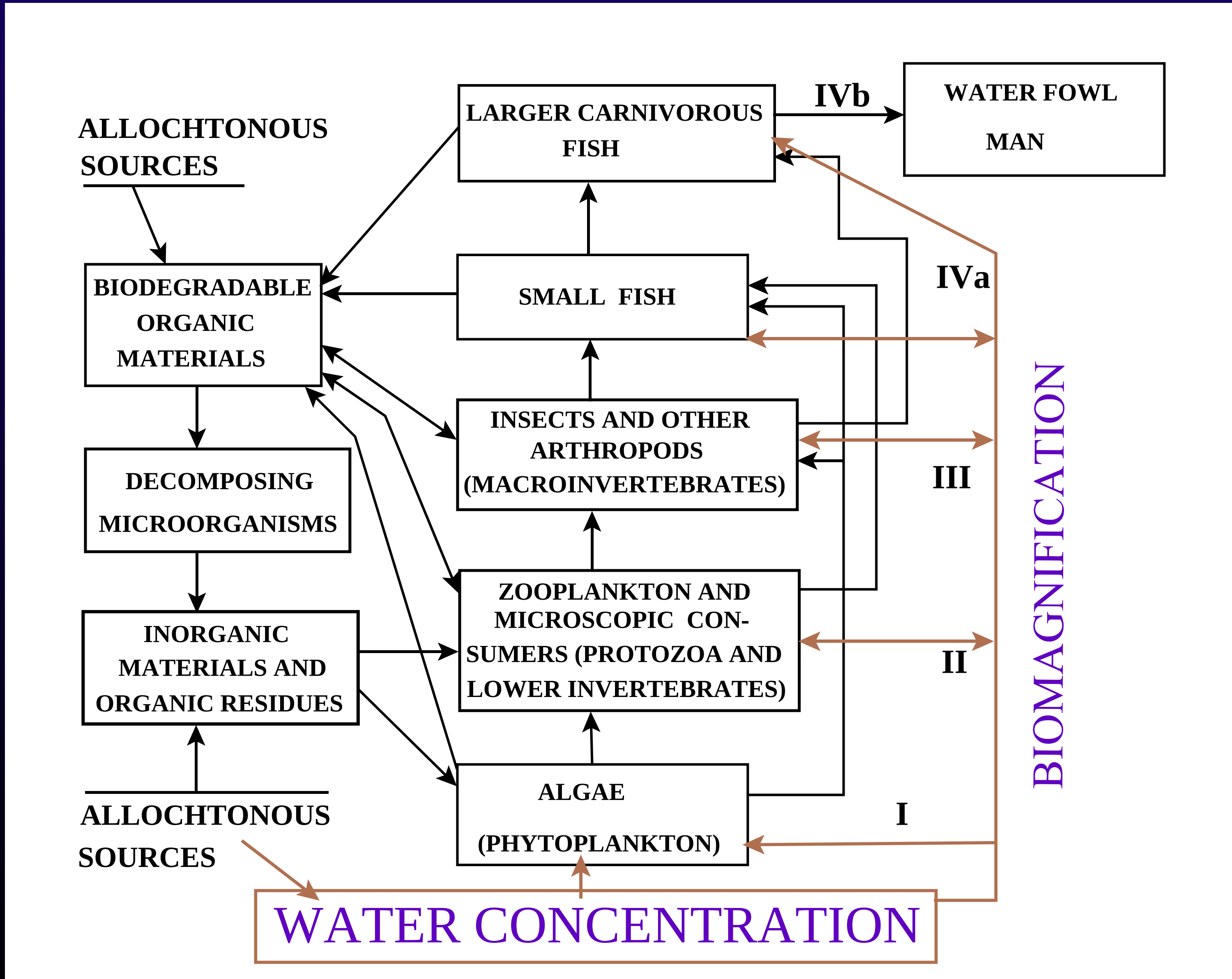


ACUTE TOXICITY
CHRONIC TOXICITY
CONCENTRATION , µg/l
1000
100
10
1
0.1
5
4
3
Monte Carlo calculated
Reach 3
3 - Pt. Washington Rd.
4 - North Av. Dam
5 - CSO data
2
5
10
20
30
40
50
60
70
80
90
95
98
99.5
99.9
CUMULATIVE PROBABILITY (% ≤)



Cd concentration, µg/l
4.95
4.9
4.85
4.8
4.75
4.7
4.65
4.6
4.55
0
500
1000
1500
2000
2500
3000
3500
4000
Time, days
With CSO
Without CSO

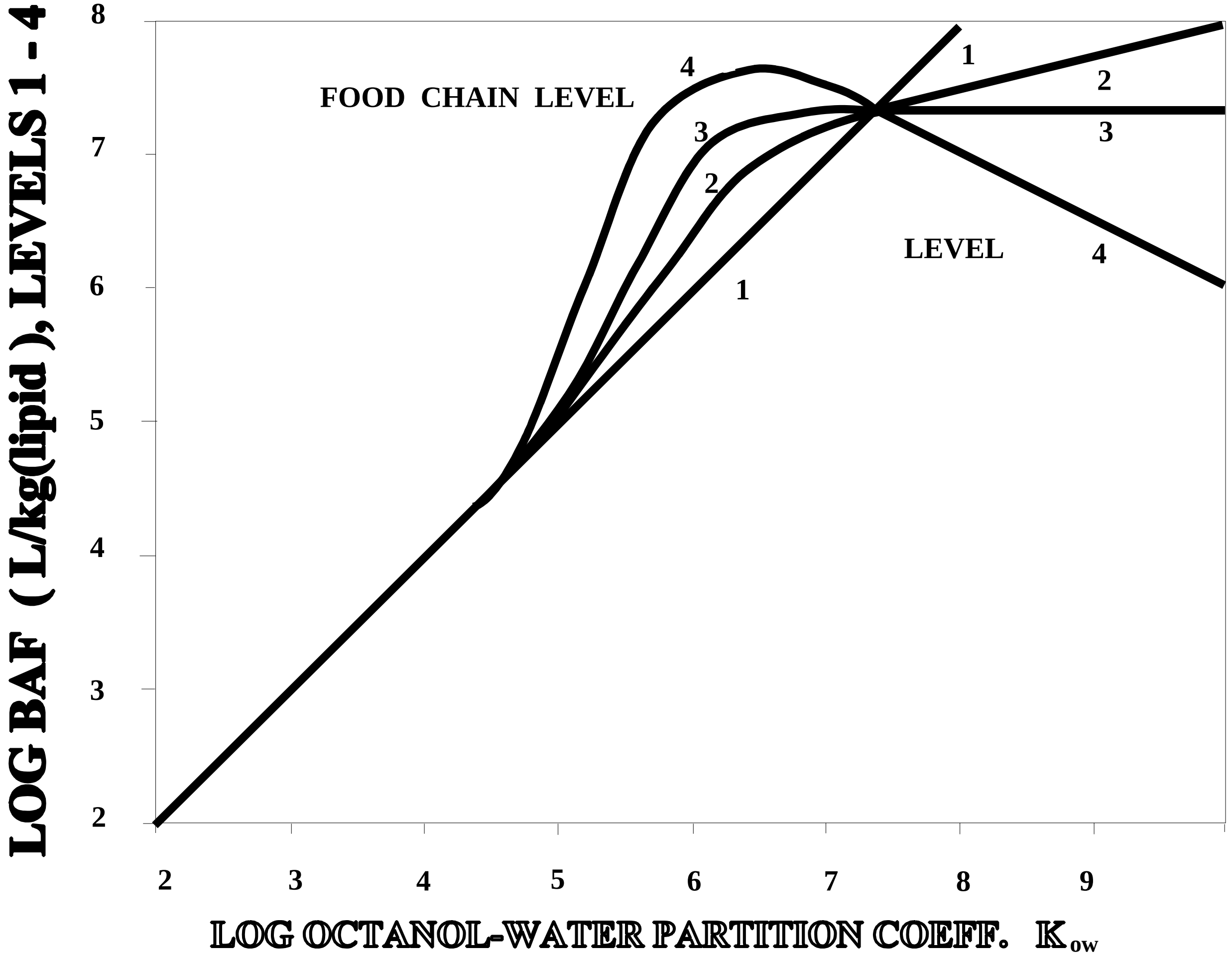
FOOD WEB PROPAGATION



BIOMAGNIFICATION

Concentrations of the toxic compounds increase in the fatty tissues (lipid) of organisms with each trophic level

Body buildup= intake - epuration



C(µg/g of lipid) = BAFx C(µg/L in water)

MODELS CAPABLE TO SIMULATE FATE OF TOXICS

DYNTOX	River	Far field	Organics, metals
WASP4	Lake, river Estuary	Far field	Organics, metals
HSP-F	River	Far field	Organics, metals
MINTEQUA2	Lake,river Estuary		Metals