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

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
c/o INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS 34100 TRIESTE (ITALY) VIA GRIGNANO, 9 (ADRIATICO PALACE) P.O. BOX 586 TELEPHONE 040-224572 TELEFAX 040-224575 TELEX 460449 APH I

SMR.648 - 3

SECOND AUTUMN WORKSHOP ON MATHEMATICAL ECOLOGY

(2 - 20 November 1992)

"Water Sediment Interactions"

D.M. Di Toro
Environmental Engineering Department
Manhattan College
Riverdale, Bronx
New York, NY 10471
U.S.A.

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

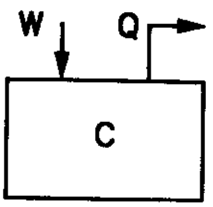
Second Annual Workshop on
Mathematical Ecology
November 1992

WATER SEDIMENT INTERACTIONS

Dominic M. Di Toro

Research Professor
Manhattan College
Bronx, New York 10471

1. Mass Balance: Sources = Losses



   A. Source: Input – W (kg/day)

   B. Loss: Outflow – Q (m3/day)

      Rate of mass loss – Q (m3/day) * C (kg/m3)

   C. Mass Balance Equation:

      Sources (kg/d) = Losses (kg/d)

      W (kg/d) = Q (m3/d) C (kg/m3)

      C = W/Q

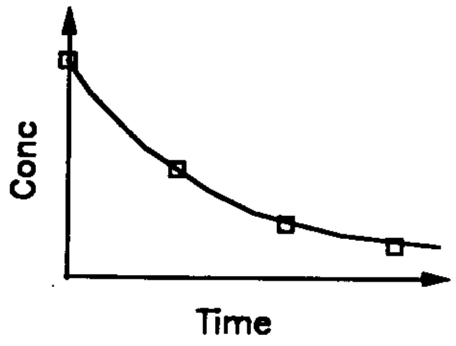
2. Loss via Reaction

   A. Mechanisms: Hydrolysis, Photolysis, Biodegradation

   B. Reaction Rate – 1st order decay

      Half Life: One half lost each t_h days

$C(0) = C_i$
$C(t_h) = C_i/2$
$c(2t_h) = C_i/4$
...



C. Equation

$$C(t) = C_i \ / \ 2^{t/t_h} = C_i \ 2^{(-t/t_h)}$$

Identity: $2 = \exp[\ln(2)]$

Therefore:

$$C(t) = C_i \ \exp(-t \ln(2)/t_h)$$

Define:

$$K = \ln(2) \ / \ t_h$$

Hence:

$$C(t) = C_i \ \exp(-Kt)$$

Example:

Half life = 10 days.
K = 0.0693 /day

3. Mass Balance with Outflow and Decay

A. Loss via decay – kg/d

Mass: V (m3) c(t) (kg/m3)

B. Rate of mass change: $V \ dC \ / \ dt$

$$C(t) = C_i \ \exp(-Kt)$$

Therefore

$$V \ dC \ / \ dt = V \ [\ C_i \ \exp(-Kt) \ (-K) \ ]$$

$$= - \underset{\nwarrow \ \text{Mass Loss via Decay}}{K V C}$$

C. Mass balance:

$$W = Q\,C + K\,V\,C$$

So That:

$$C = W / (Q + K\,V)$$

$$= \frac{W/Q}{(1 + K\,t_o)}$$

Important Quantity

Where:

$$t_o = V/Q$$

$$= \text{hydraulic residence time}$$

4. Partitioning

A. Adsorption – Desorption Reaction

Dissolved

Sorbed

$$C + M \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} C{=}M$$

Particle

B. Mass Action

Partition Coefficient

$$\frac{[\,C{=}M\,]}{[\,C\,][\,M\,]} = \frac{k_{ads}}{k_{des}} = P$$

C. Particulate and Dissolved Concentrations

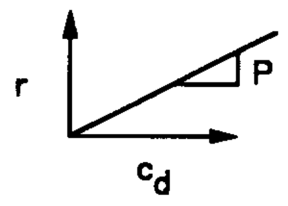
$$\frac{[\,C{=}M\,]}{[\,C\,]\,[\,M\,]} = \frac{k_{ads}}{k_{des}} = P$$

Dissolved C_d

Particulate: $r = \dfrac{(ug/L)}{(g/L)} = (ug/g)$

D. Isotherm

$$r = P\ c_d$$



E. Fraction Dissolved: f_d

$$C_T = [\,C{=}M\,] + [\,C\,]$$
$$= m\,r + c_d$$
$$= m\,P\,c_d + c_d = (\,m\,P + 1\,)\,c_d$$

Therefore:

$$f_d = c_d\,/\,c_T = 1\,/\,(\,1 + m\,P\,)$$

Fraction Particulate

$$f_p = 1 - f_d$$

5. Reaction & Partitioning

A. Hydrolysis, Photolysis: $K V f_d C_T$

B. Mass Balance

$$W = Q C_T + K V f_d C_T$$

Therefore:

$$C_T = \frac{W/Q}{1 + K f_d t_o}$$

Reaction Rate Modified
by dissolved fraction

6. Settling

A. Settling velocity: $w_a = 0.1 - 10$ m/d

B. Chemical Flux

$$w_a \text{ (m/d) } A \text{ (m2) } f_p C_T \text{ (kg/m3) } = \text{ (kg/d)}$$

C. Mass Balance

$$W = Q C_T + K V f_d C_T + w_a A f_p C_T$$

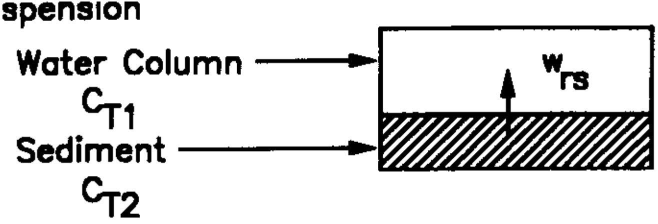
So That: (H = V/A)

$$C_T = \frac{W/Q}{1 + K f_d t_o + w_a \backslash H \; f_p t_o}$$

Loss by Decay

Loss by Settling

7. Resuspension



A. Resuspension velocity: w_{rs} (mm/yr)

B. Chemical Flux

w_{rs} (m/d) A (m2) $f_{p2}\,C_{T2}$

C. Mass Balance

$$w_a f_{p1} C_{T1} = w_{rs} f_{p2} C_{T2}$$

So That:

$$C_{T2} = w_a f_{p1} C_{T1} / w_{rs} f_{p2}$$

D. Particulate Concentration Ratio

$$C_{T2} = w_a f_{p1} C_{T1} / w_{rs} f_{p2}$$

Particulate Concentrations

$r_1 = f_{p1}\,C_{T1}/m_1 \qquad r_2 = f_{p2}\,C_{T2}/m_2$

Therefore:

$r_2/r_1 = w_a m_1 / w_{rs} m_2$

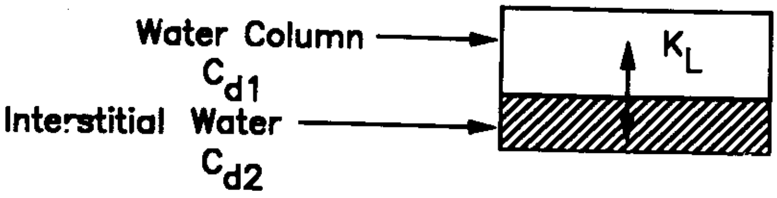
Particle Mass Balance

$$w_a m_1 = w_{rs} m_2$$

So That:

$r_2/r_1 = 1$ (NEAT !!)

8. Diffusion

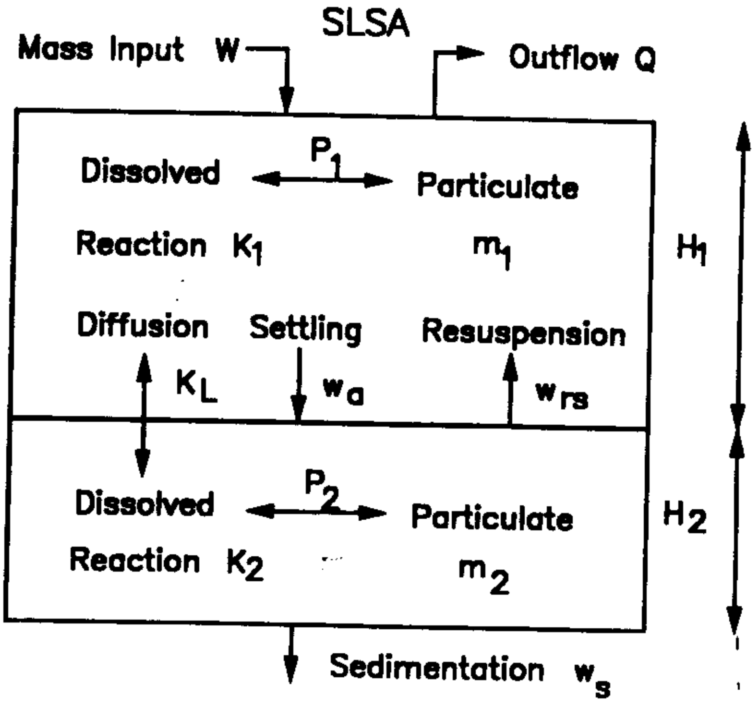


A. Diffusion flux

$$D/H\ (c_{d2} - c_{d1})$$

Mass Transfer Coefficient: K_L
(cm/day)

9. SLSA Definitions



SLSA

Solution:

$$C_{T1} = \frac{W/Q}{1 + K_T t_o}$$

Water Column Equivalent Removal Rate K_T

$$K_T = K_1 + B\,(r_2/r_1)(K_2 + K_s) \qquad ; K_s = w_s/H_2$$

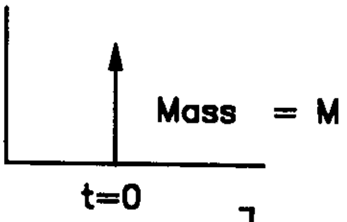
Where:

$$B = \frac{m_2\,H_2\,f_{p1}}{m_1\,H_1\,f_{p2}} \quad \text{Capacity Factor}$$

And:

$$\frac{r_2}{r_1} = \frac{(w_{rs} + w_s)\,f_{p2} + K_L(P_2/P_1)\,f_{d2}}{(w_{rs} + w_s)\,f_{p2} + K_L\,f_{d2} + K_2 H_2}$$

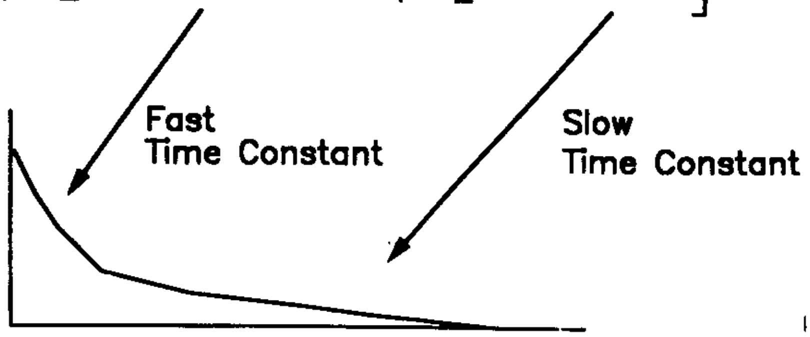
Instantaneous Release into Water Column



Solution:

$$C_{T1}(t) = M/V \,*$$

$$\left[\frac{s_1}{s_1+s_2}\exp(-g_1 t) + \frac{s_2}{s_1+s_2}\exp(-g_2 t)\right]$$



Coefficients and Exponents

Sum of Losses:

$$s_1 = K_1 + (w_a f_{p1} + K_L f_{d1}) / H_1 \qquad \downarrow$$

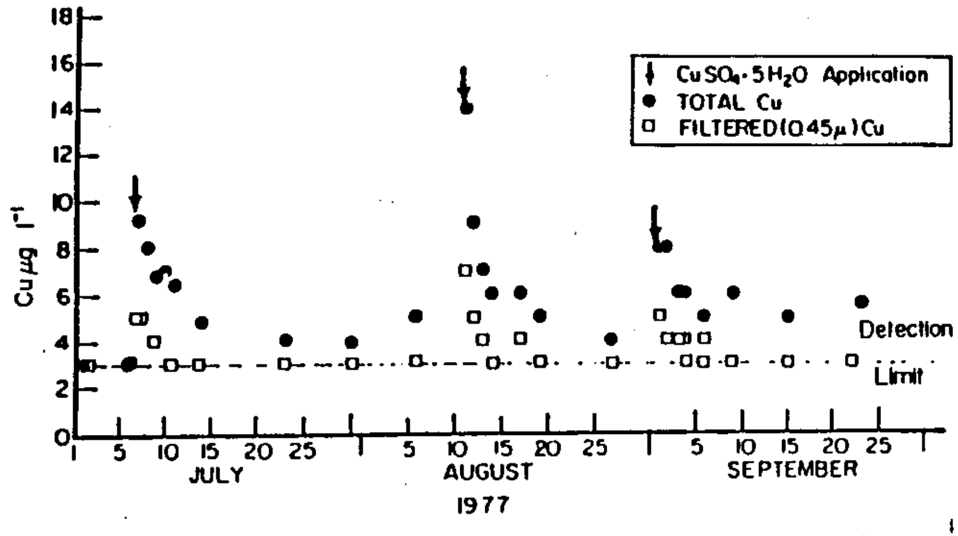
$$s_2 = K_2 + \left[(w_{rs} + w_s) f_{p2} + K_L f_{d2})\right] / H_2 \qquad \uparrow$$

Approximate Time Constants

$$g_1 = s_1 + s_2 + 1/t_o \quad \text{(fast)} \quad \uparrow + \downarrow$$

$$g_2 = \frac{s_2}{s_1 + s_2 + 1/t_o} (K_T + 1/t_o) \quad \text{(slow)} \quad \frac{\uparrow}{\uparrow + \downarrow}$$

Whole lake responses to low level copper sulfate treatment



Temporal trends in upper water (average of 0.25, 2.5 and 5.0 m values) copper for summer, 1977.

Reference: Effler, S.W., Litten, S., Field, S.D., Tong-Ngork, T., Hale, F., Meyer, M. and Quirck, M. (1980): Whole Lake Responses to Low Level Copper Sulfate Treatment. Water. Res. 14: pp. 1489-1499.

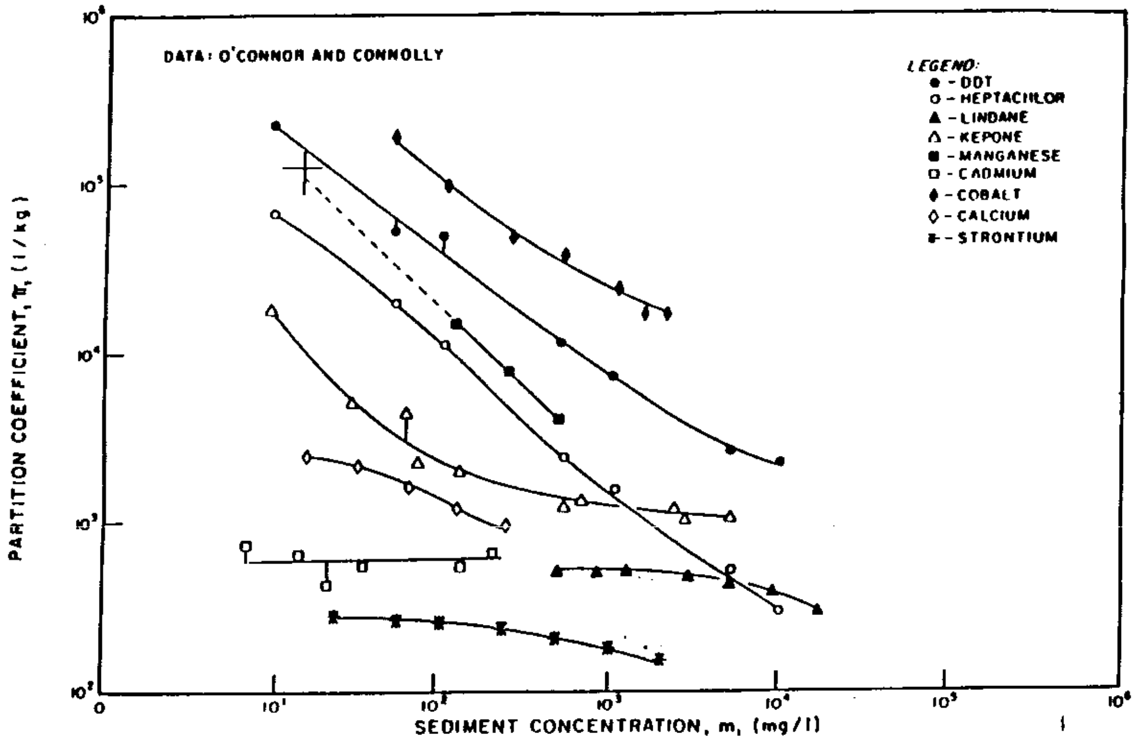


FIGURE 5-12. VARIATION OF PARTITION COEFFICIENTS WITH SOLID CONCENTRATION

4. Particle Interaction Model (PIM)

A. Adsorption – Desorption $C + M \underset{k_{des}}{\overset{k_{ads}}{\longleftrightarrow}} C{=}M$

B. Particle Induced Desorption $C{=}M + M \xrightarrow{k_{pd}} C + 2M$

C. PIM $nu_x = 1.4$

$$P = \frac{K_{ow}\, f_{oc}}{1 + m\, K_{ow}\, f_{oc} / nu_x}$$

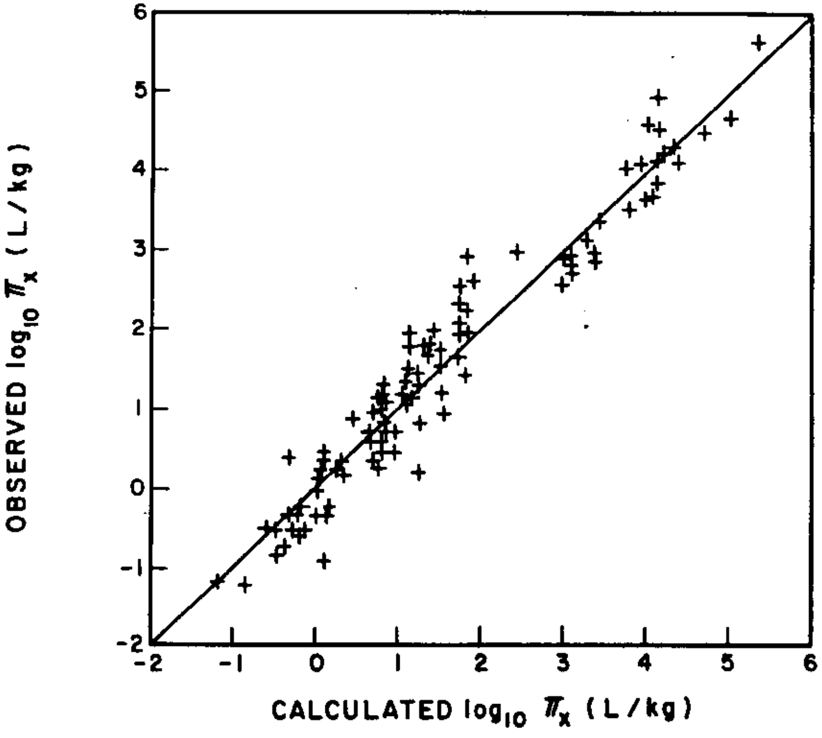
D. Asymptotic Behavior

$P \rightarrow K_{ow}\, f_{oc}$ for m small

$P \rightarrow nu_x / m$ for m large

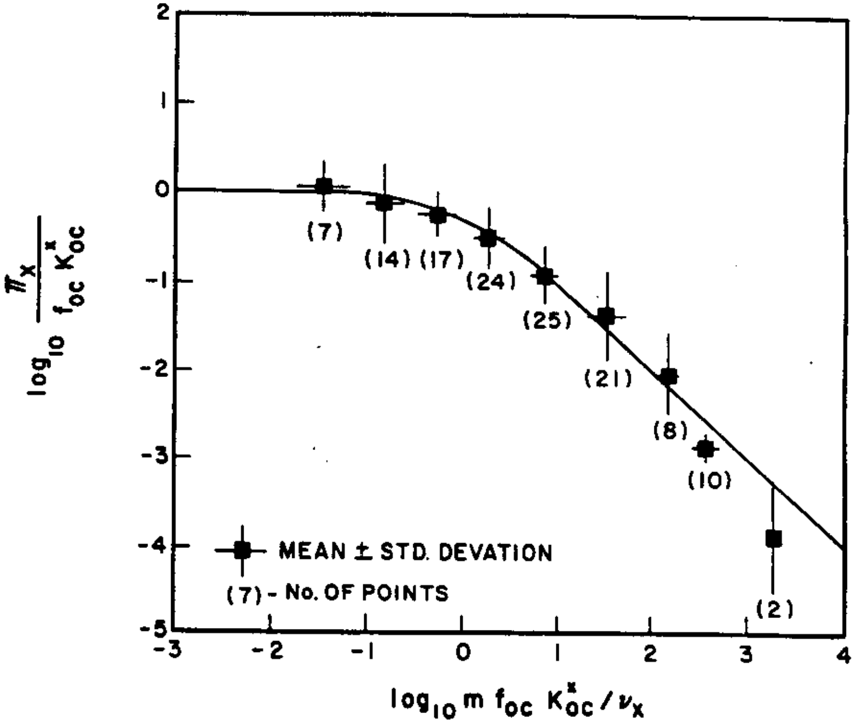
REVERSIBLE COMPONENT PARTITION COEFFICIENTS
COMPARISON TO PARTICLE INTERACTION MODEL
NEUTRAL ORGANIC CHEMICALS

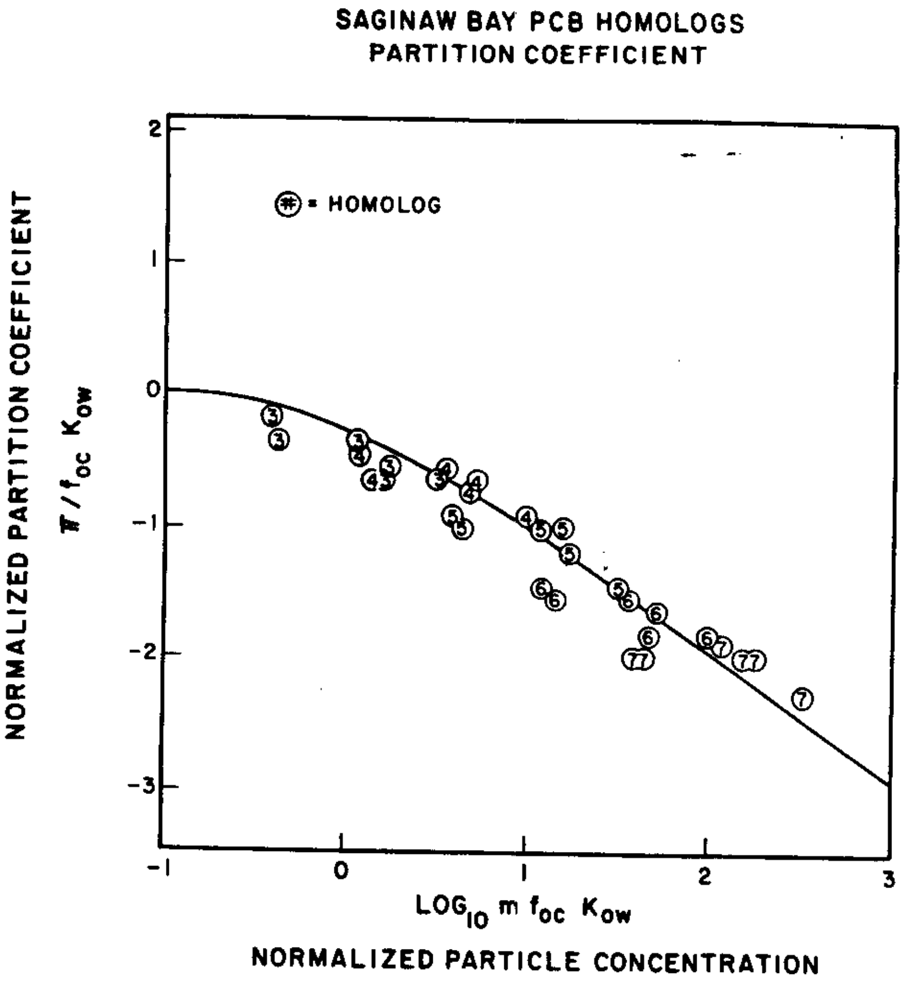
$\nu_x = 1.40 \quad \log_{10} K_{oc}^{x} = 0.00028 + 0.983 \log_{10} K_{ow}$



REVERSIBLE COMPONENT PARTITION COEFFICIENTS
COMPARISON TO PARTICLE INTERACTION MODEL
NEUTRAL ORGANIC CHEMICALS

$\nu_x = 1.40 \quad \log_{10} K_{oc}^{x} = 0.00028 + 0.983 \log_{10} K_{ow}$





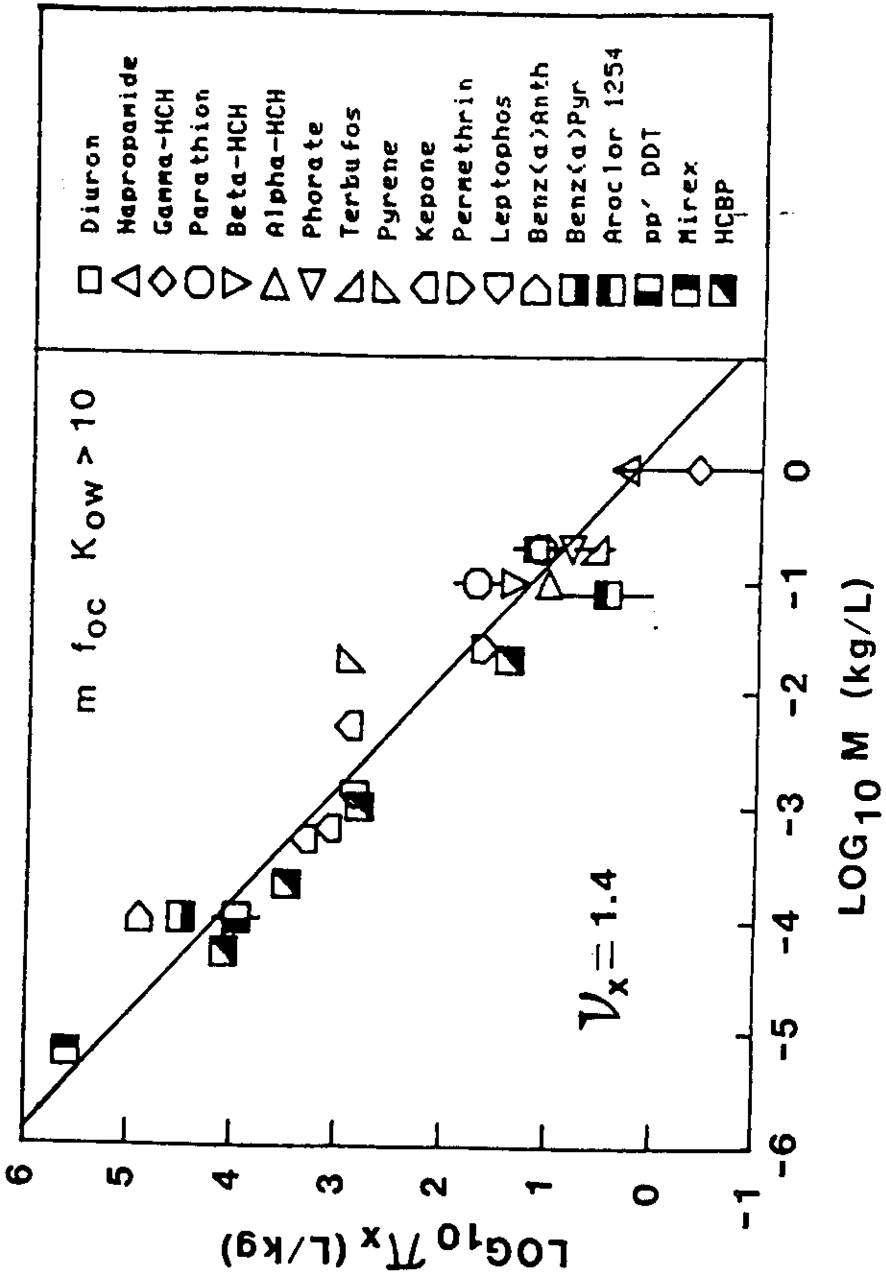


Fig. 9. The high particle concentration limit. π_x as a function of m only.

```
              S L S A
       SLSA EXAMPLE DECK - LINDANE


         SIMPLE LAKE ANALYSIS

        PHYSICAL PARAMETERS

       FLOW............. 4.245E+00 M**3/SEC
       LOAD............. 1.000E+00 KG/DAY
       VOLUME........... 3.680E+07 M**3
       DETENTION TIME... 1.003E+02 DAYS
```

```
              S L S A
       SLSA EXAMPLE DECK - LINDANE

   WATER COLUMN                          SEDIMENT LAYER

   DEPTH...........     3.90 METERS        .05 METERS
   SUSP SOLIDS......       24. MG/L     750000. MG/L
   SETTLING VEL.....     2.140 M/DAY        10.0 MM/YR

   RESUSP VEL.......      15.0 MM/YR
   DIFF EXCH COEFF..      50.0 CM/DAY
```

```
                         S L S A
                SLSA EXAMPLE DECK -- LINDANE


               CHEMICAL/PHYSICAL PARAMETERS
                    FOR    LINDANE

       WATER COLUMN                    SEDIMENT LAYER
     ----------------               ----------------
     PARTITION COEFF                PARTITION COEFF
     (P1)............ 2.500E+02 L/KG  (P2)............ 5.000E+01 L/KG

     PHASE FRACTIONS                 PHASE FRACTIONS
     PARTICULATE.....   .00596      PARTICULATE.....   .97403
     DISSOLVED.......   .99404      DISSOLVED.......   .02597


     HYDROLYSIS RATE..   .00250 /DAY  HYDROLYSIS RATE..   .00250 /DAY
     PHOTOLYSIS RATE..   .00026 /DAY
     VOLATILITY RATE..   .00026 /DAY

     TOTAL REMOVAL                  TOTAL REMOVAL
     RATE (K1).......   .00302 /DAY  RATE (K2).......   .00250 /DAY
```

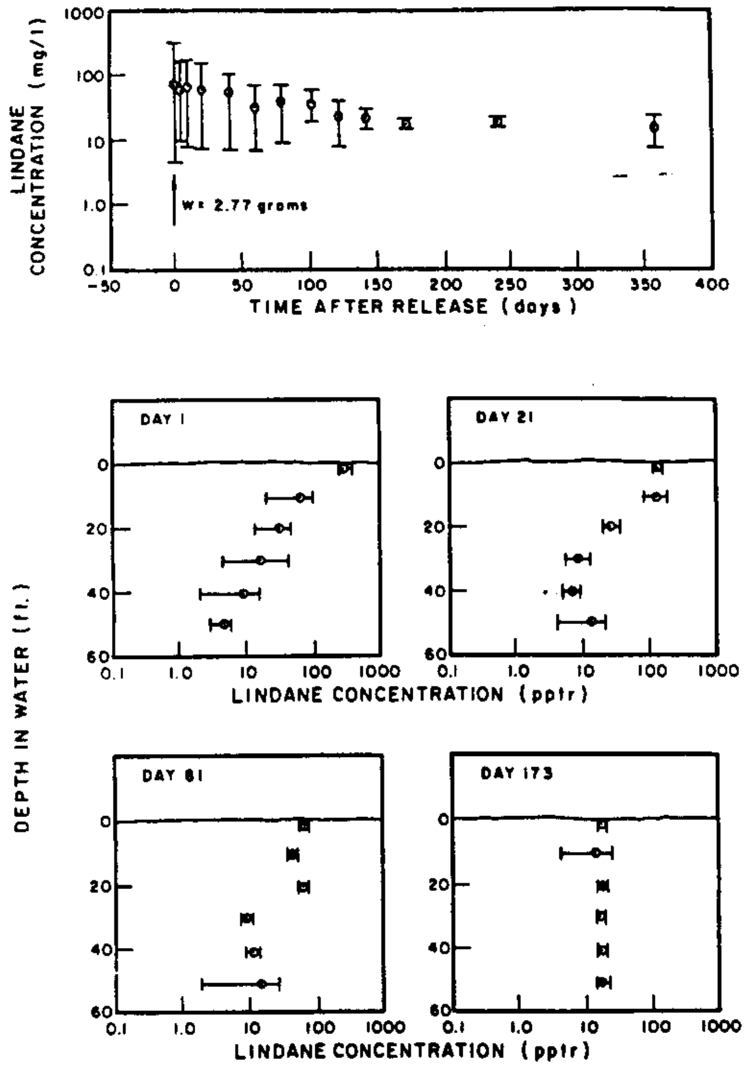
```
              S L S A
     SLSA EXAMPLE DECK -- LINDANE


   STEADY STATE SOLUTION

   CT1 = 1.860E+00 UG/L    CT2 = 7.186E+01 UG/L
   FD1 =   .99404          FD2 =   .02597
   FP1 =   .00596          FP2 =   .97403

   DIAGNOSIS                      VELOCITIES            RATES
                                    MM/YR                /DAY
   WATER COLUMN SETTLING......  (WA) 781250.
   SEDIMENTATION.............  (WS)    10.          (KS)  .00049
   RESUSPENSION..............  (WRS)    15.
   DIFFUSIVE EXCH COEFF.......  (KL) 182500.
   WATER COLUMN REMOVAL.......                           (K1)  .00302
   SEDIMENT LAYER REMOVAL.....                           (K2)  .00250

   SEDIMENT CAPACITY FACTOR.....
                                        M2*H2*FP1
                                 BETA = ------------- =    2.699
                                        M1*H1*FP2
```

```
RATIO OF PARTICULATE CONCENTRATIONS.....

  R2    (WRS+WS)*FP2 + KL*(P2/P1)*FD2
 --- = ----------------------------
  R1    (WRS+WS)*FP2 + KL*FD2 + K2*H2

  R2      (24.35) +  (948)
 ---- = ------------------------------- = 0.202
  R1    ( 24.35) +  (4740)  +  (50.19)


  TOTAL APPARENT REMOVAL RATE.....

  KT = K1 + BETA*R2/R1*(K2+KS)   /DAY

.0048 =   .00302 + 2.6988* .202*(  .00250 +  .00049)
```

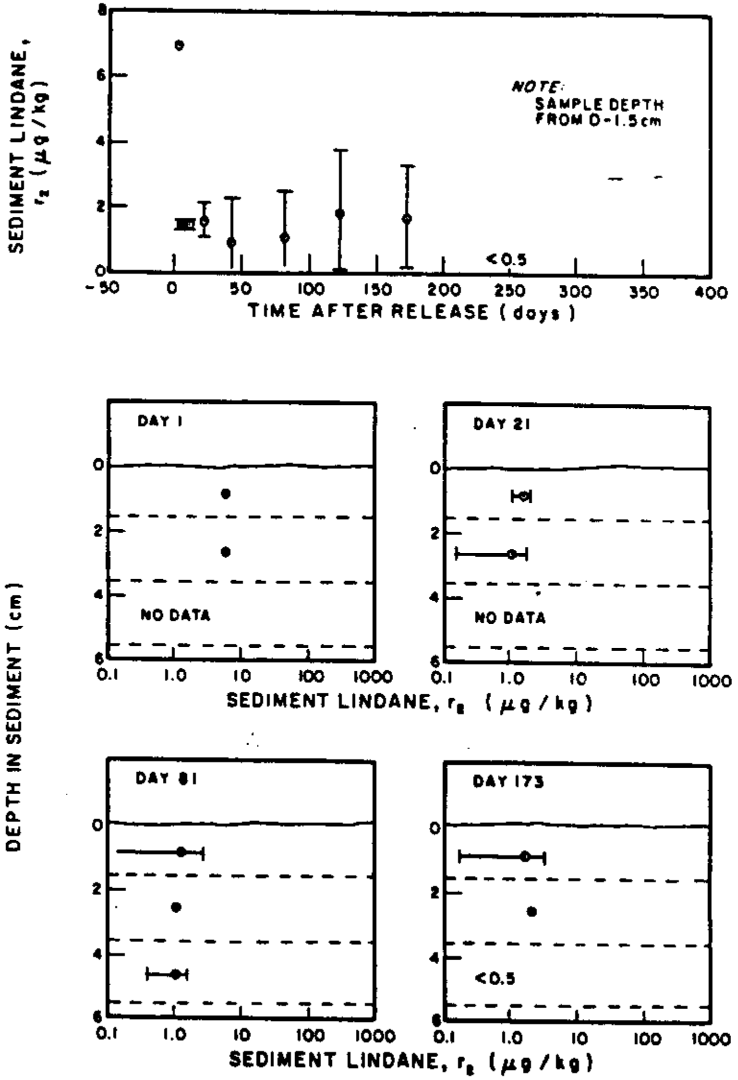
```
               S L S A
      SLSA EXAMPLE DECK - LINDANE

         TIME VARIABLE BEHAVIOR

  TIME    CT1(T)/CT1(SS)    CT2(T)/CT2(SS)
 (DAYS)        (%)               (%)
  29.17       25.00             21.95
  72.45       50.00             47.97
 170.27       80.00             79.19
 244.27       90.00             89.59
```

```
          DIAGNOSIS

MAGNITUDES:  WATER COLUMN REACTION AND TRANSPORT      (/DAY)

    K1 =          .00302     WA*FP1/H1 =    .00327
    KL*FD1/H1 =   .12744

 ----  S1 = K1 + WA*FP1/H1 + KL*FD1/H1 =  .13373

MAGNITUDES:  SEDIMENT LAYER REACTION AND TRANSPORT     (/DAY)

    K2 =          .00250     WS*FP2/H2 =    .00049
    KL*FD2/H2 =   .23613      WRS*FP2/H2 =    .00073

 ----  S2 = K2 + WS*FP2/H2 + KL*FD2/H2 + WRS*FP2/H2 =  .23984

ST = S1 + S2 =  .37357     ST + 1/T0 =  .37357 +  .00997 =  .38354

EXPONENTS:     (/DAY)
    G1 (EXACT) =                   .37417
    G1 (APPROX) = ST + 1/T0 =   .38354
    G2 (EXACT) =                                     .00937
    G2 (APPROX) = S2/(ST + 1/T0) * (KT + 1/T0) =   .00914
```

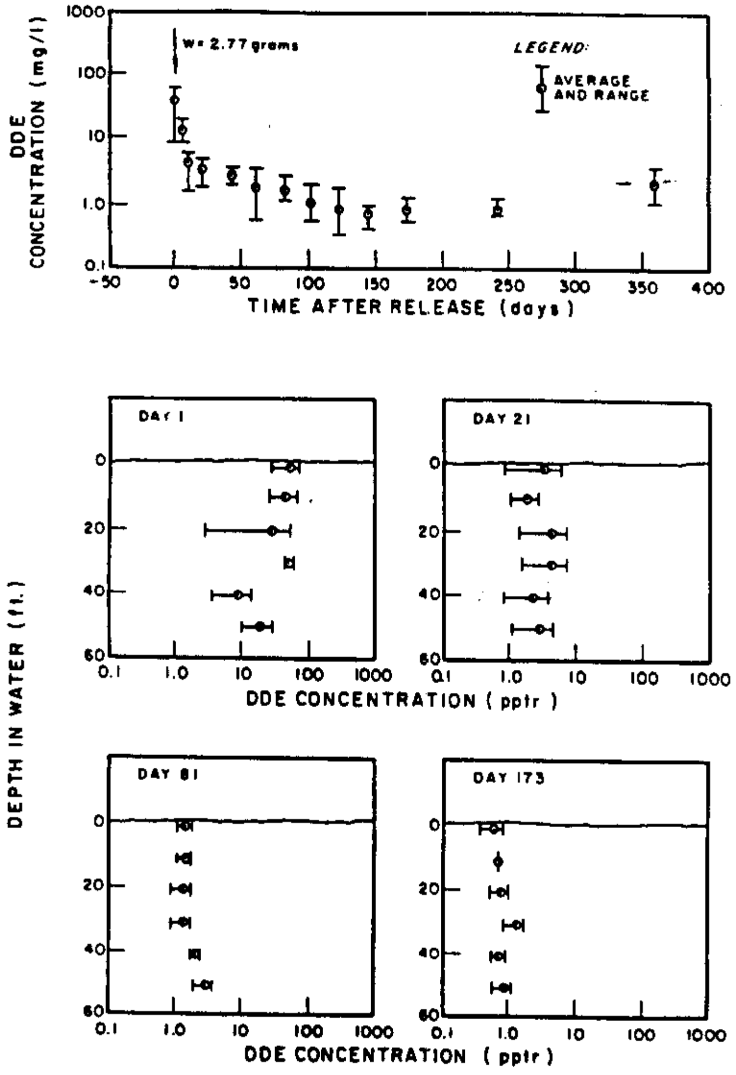
```
   TIME     - - - W A T E R   C O L U M N - - -
  (DAYS)                  (UG/L)
              TOTAL       DISSOLVED    PARTICULATE

    10.0    2.5435E-02    2.5283E-02    1.5170E-04
    20.0    4.8107E-02    4.7820E-02    2.8692E-04
    30.0    6.8827E-02    6.8416E-02    4.1050E-04
    40.0    8.8158E-02    8.7632E-02    5.2579E-04
    50.0    1.0649E-01    1.0585E-01    6.3510E-04
    60.0    1.2408E-01    1.2334E-01    7.4002E-04
    70.0    1.4111E-01    1.4027E-01    8.4163E-04
    80.0    1.5773E-01    1.5678E-01    9.4071E-04
    90.0    1.7400E-01    1.7296E-01    1.0378E-03
   100.0    1.8999E-01    1.8886E-01    1.1331E-03
   110.0    2.0575E-01    2.0452E-01    1.2271E-03
   400.0    5.9952E-01    5.9594E-01    3.5758E-03
   800.0    9.9325E-01    9.8733E-01    5.9240E-03
  1200.0    1.2640E+00    1.2564E+00    7.5385E-03
```



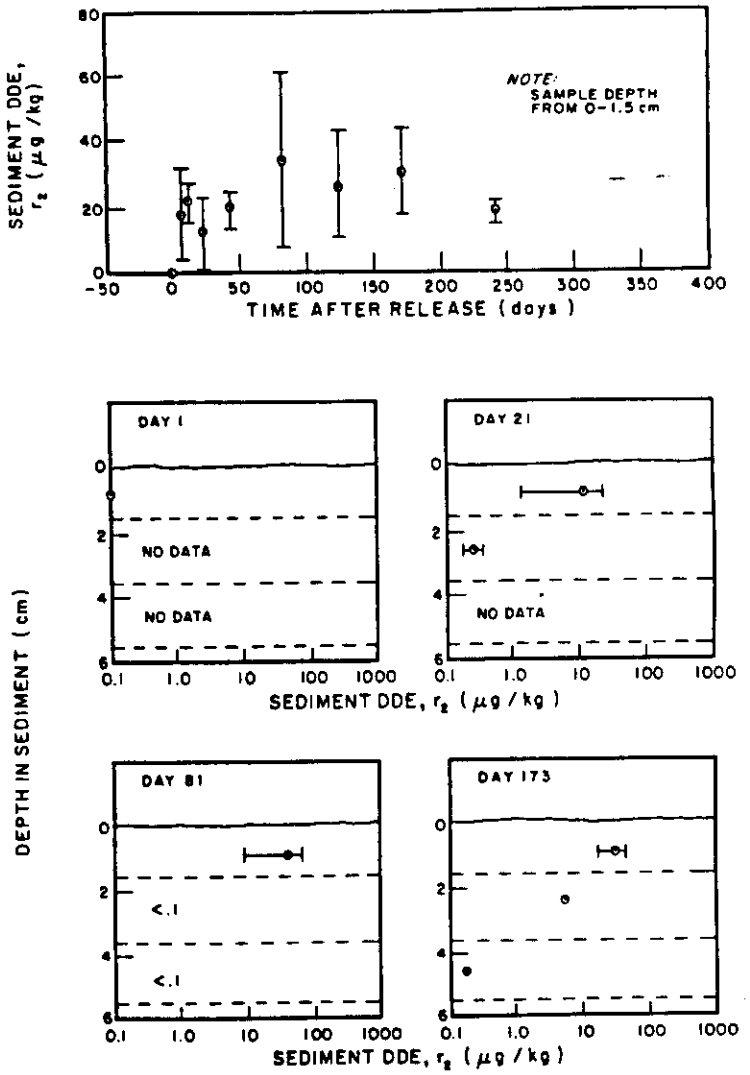
DATA: WAYBRANT, 1973



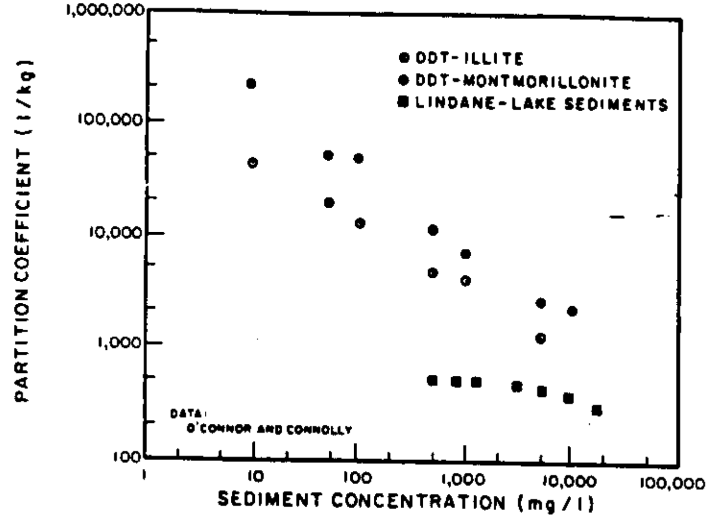
DATA: WAYBRANT, 1973

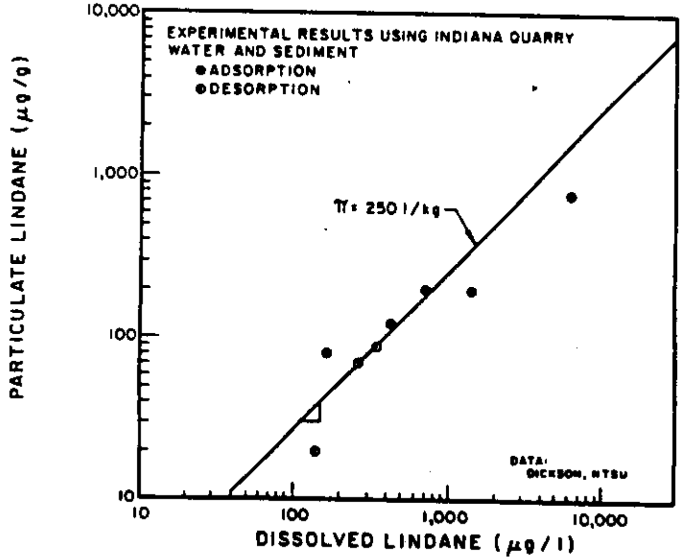


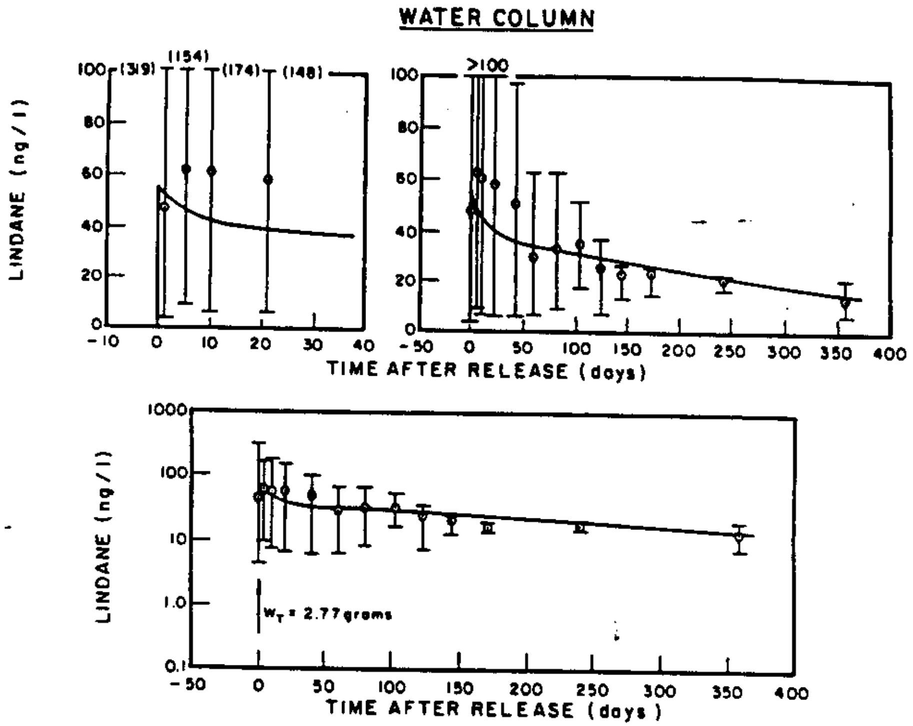
DATA: WAYBRANT, 1973

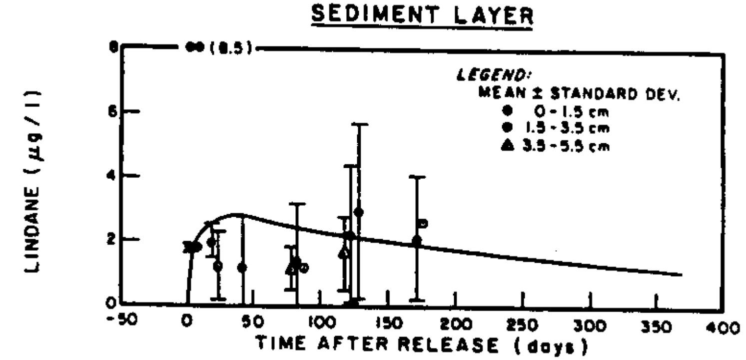


DATA: WAYBRANT, 1973

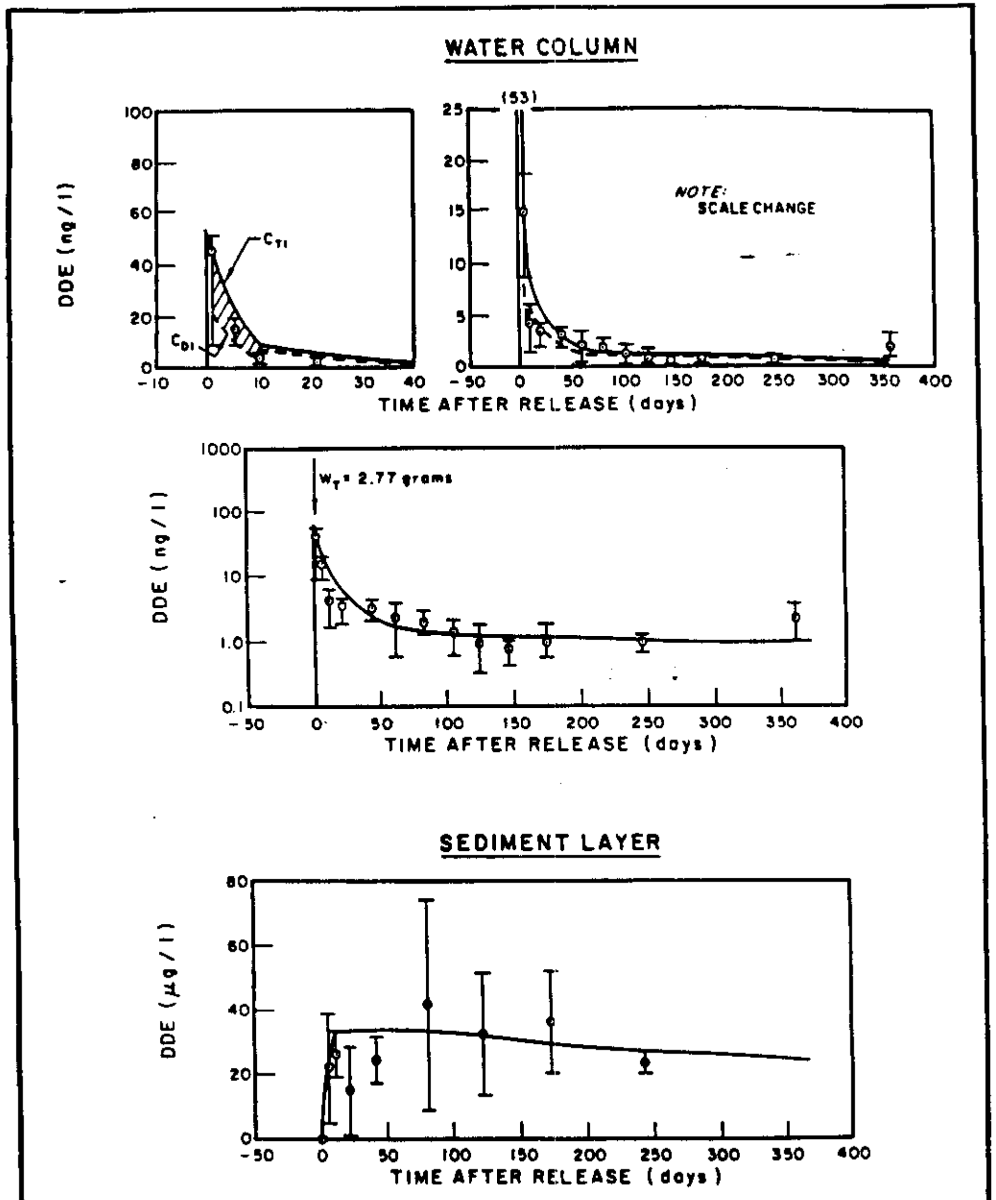




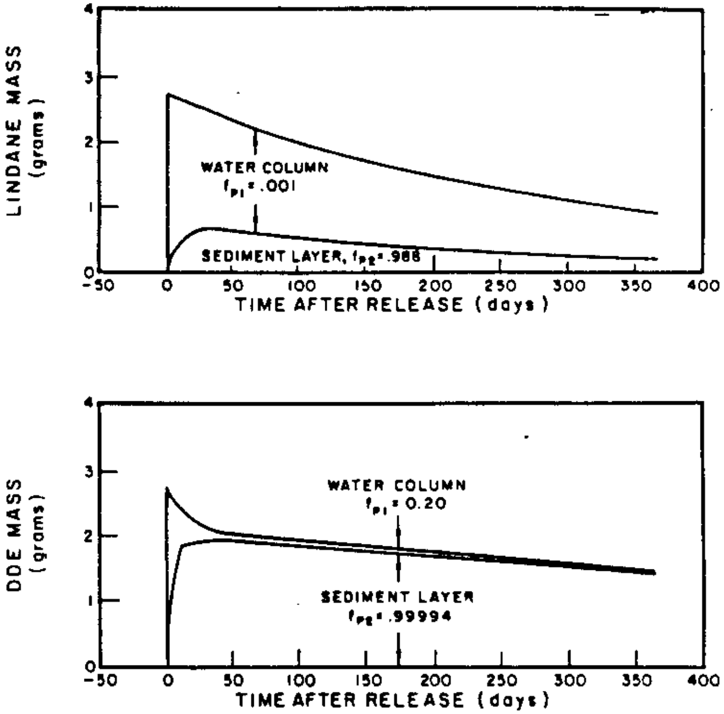


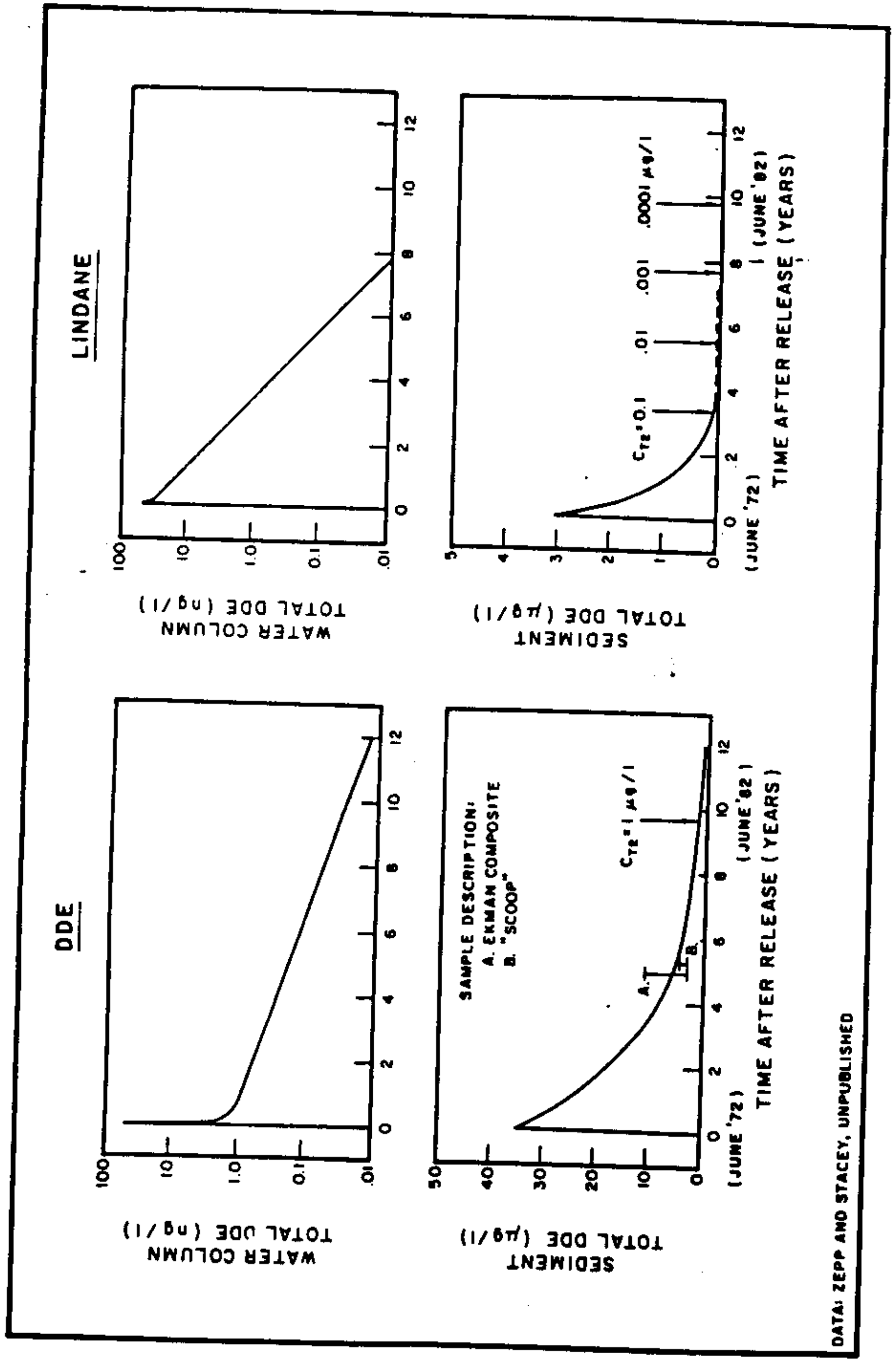


DATA: WAYBRANT, 1973

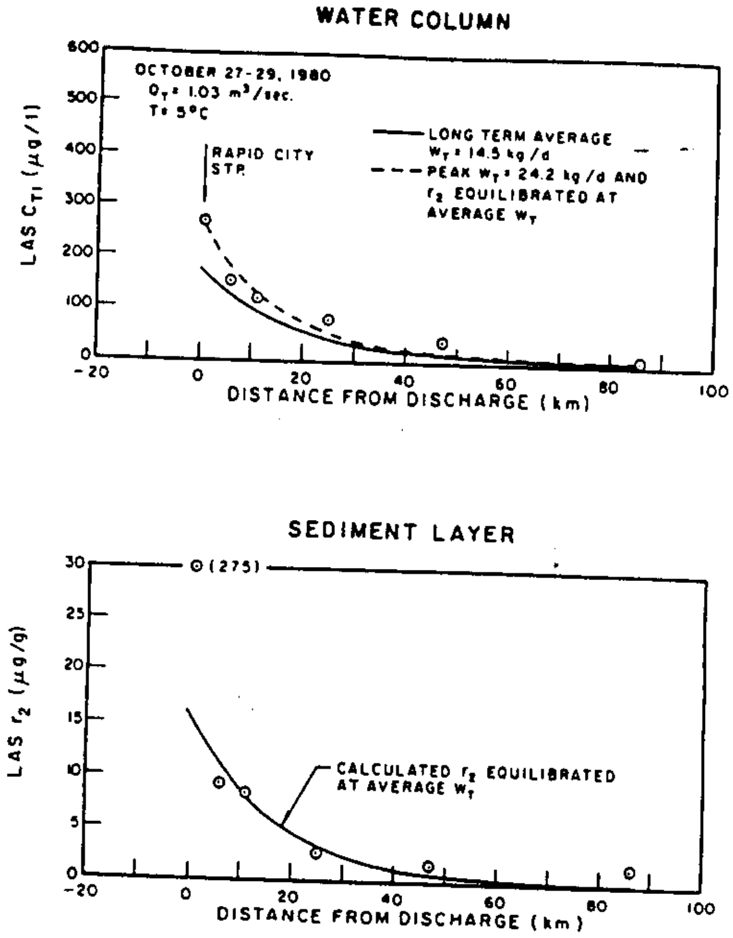


DATA: WAYBRANT, 1973





DATA: ZEPP AND STACEY, UNPUBLISHED



From HydroQual (1983)

APPLICATION TO LAS IN A STREAM

The required input is as follows:

Card 1: Title Card

```
        1                                           80
(1)     ***** THIS IS A SAMPLE RUN FOR SLSA *****
```

FORMAT (80A1)

TITLE - any 80 character alphanumeric character string may be used to identify the model run

Card 2: Water Body Type

```
        1    6
(2)     WBODY
```

FORMAT (A6)

WBODY - indicates whether the receiving water body is a lake or stream

- = LAKE, the receiving water body is a lake
- = STREAM, the receiving water body is a stream

Cards 3a and 3b: Physical Parameters

The physical parameters to be read as input depend upon the water body type. If the user is analyzing receiving water response in a lake, the required input is described immediately below; if the user is analyzing a stream response the required input is described under Stream Parameters.

Lake Parameters

```
          10     20     30     40     50     60     70     80
(3a)       Q    VOL     WK     H1     H2     M1     M2     KL
```

FORMAT (8F10.0)

```
          10     20
(3b)     WRS     WS
```

FORMAT (2F10.0)

Q = the net advective flow rate, in cubic meters/sec.
VOL = volume of lake, in cubic meters
WK = loading rate, in kg/day
H1 = water column depth, in meters
H2 = sediment layer depth, in meters
M1 = solids concentration in the water column, in mg/l

M2 - solids concentration in the sediment layer, in mg/l
KL - diffusive exchange coefficient, in cm/day
WRS - resuspension velocity, in mm/yr
WS - sedimentation velocity, in mm/yr

Stream Parameters

(3a)

10	20	30	40	50	60	70	80
Q	XA	WK	H1	H2	M1	M2	KL

FORMAT (8F10.0)

(3b)

10	20	30	40
WRS	WS	XTOT	DELTAX

FORMAT (5F10.0)

Q - net advective flow rate, in cubic meters/sec
XA - cross-sectional area of stream, in square meters
WK - loading rate, in kg/day
H1 - water column depth, in meters
H2 - sediment layer depth, in meters
M1 - solids concentration in the water column, in mg/l
M2 - solids concentration in the sediment layer, in mg/l
KL - diffusive exchange coefficient, in cm/day
WRS - resuspension velocity, in mm/yr
WS - sedimentation velocity in mm/yr
XTOT - total distance downstream of point source discharge for which receiving water response is to be determined, in km
DELTAX - desired spatial distance for displaying receiving water response to the point source load, in km.

Cards 4a and4b: Chemical Parameters

(4a)

1 40	50	60	70	80
CHEMICAL NAME	PIE1	PIE2	KHYDR1	KHYDR2

FORMAT (40A10.0)

(4b)

10	20	30	40	50	60
KOXID1	KOXID2	KBIOL1	KBIOL2	KPHOT1	KVOLA1

FORMAT (6F10.0)

CHEMNA - 1 to 40 alphanumeric character descriptor for the chemical whose water quality response is being analyzed.
PIE1 - water column partition coefficient, in l/kg
PIE2 - sediment layer partition coefficient, in l/kg
KHYDR1 - rate of hydrolysis of the chemical in the water column, in /day
KHYDR2 - rate of hydrolysis of the chemical in the sediment layer, in/day
KOXID1 - rate of oxidation of the chemical in the water column, in /day
KOXID2 - rate of oxidation of the sediment layer, in /day
KBIOL1 - rate of biodegradation of the chemical in the water column, in /day

KBIOL2 - rate of biodegradation of the sediment layer, in /day
KPHOT1 - rate of photolysis (photochemical transformation) of the chemical in the water column, in /day
KVOL1 - rate of volatilization of the chemical in the water column, in /day

```
                              S L S A
                             ---------

   DEVELOPED BY HYDROQUAL,  INC.
                MAHWAH,  NJ 07430
                201-529-5151

   REFERENCE:  DITORO,D.M., O'CONNOR,D.J., THOMANN,R.V.
   "MODELING THE FATE OF CHEMICALS IN THE AQUATIC
   ENVIRONMENT", T. EDITED BY DICKSON,K.L., MAKI,A.W.,
   CAIRNS,J., ANN ARBOR SCIENCE, 1982, CHAPTER 10,
   PG. 165-189.

     SLSA EXAMPLE DECK - LINDANE


                 SIMPLE LAKE ANALYSIS

                 PHYSICAL PARAMETERS
                 -------------------
                 FLOW............. 4.245E+00 M**3/SEC
                 LOAD............. 1.000E+00 KG/DAY
                 VOLUME........... 3.680E+07 M**3
                 DETENTION TIME... 1.003E+02 DAYS


WATER COLUMN                             SEDIMENT LAYER
------------                             --------------
DEPTH............      3.90 METERS       DEPTH............         .05 METERS
SUSP SOLIDS......       24. MG/L         SUSP SOLIDS......   750000. MG/L
SETTLING VEL.....     2.140 M/DAY        SEDIMENT VEL.....      10.0 MM/YR

RESUSP VEL.......      15.0 MM/YR
DIFF EXCH COEFF..      50.0 CM/DAY


                 CHEMICAL/PHYSICAL PARAMETERS
                 ----------------------------
            FOR    LINDANE
                 WATER COLUMN                           SEDIMENT LAYER
                 ------------                           --------------
                 PARTITION COEFF                        PARTITION COEFF
(P1)............. 2.500E+02 L/KG         (P2)............. 5.000E+01 L/KG

PHASE FRACTIONS                          PHASE FRACTIONS
PARTICULATE......    .00596              PARTICULATE......     .97403
DISSOLVED........    .99404              DISSOLVED........     .02597


HYDROLYSIS RATE..    .00250 /DAY         HYDROLYSIS RATE..     .00250 /DAY
OXIDATION RATE...    .00000 /DAY         OXIDATION RATE...     .00000 /DAY
BIOLYSIS RATE....    .00000 /DAY         BIOLYSIS RATE....     .00000 /DAY
PHOTOLYSIS RATE..    .00026 /DAY
VOLATILITY RATE..    .00026 /DAY

TOTAL REMOVAL                            TOTAL REMOVAL
RATE (K1)........    .00302 /DAY         RATE (K2)........     .00250 /DAY
```

```
                           STEADY STATE SOLUTION
                           ---------------------

                 CT1 = 1.860E+00 UG/L      CT2 = 7.186E+01 UG/L
                 FD1 =    .99404           FD2 =    .02597
                 FP1 =    .00596           FP2 =    .97403


                              DIAGNOSIS
                              ---------

                                     VELOCITIES              RATES
                                         MM/YR                /DAY
    WATER COLUMN SETTLING......   (WA) 781250.
    SEDIMENTATION..............   (WS)     10.          (KS)  .00049
    RESUSPENSION...............  (WRS)     15.
    DIFFUSIVE EXCH COEFF.......   (KL) 182500.
    WATER COLUMN REMOVAL.......                         (K1)  .00302
    SEDIMENT LAYER REMOVAL.....                         (K2)  .00250


    SEDIMENT CAPACITY FACTOR.....

                                   M2*H2*FP1
                          BETA = ----------- =    2.699
                                   M1*H1*FP2


    RATIO OF PARTICULATE CONCENTRATIONS.....

                   R2     (WRS+WS)*FP2 + KL*(P2/P1)*FD2
                  ---- = ------------------------------
                   R1     (WRS+WS)*FP2 + KL*FD2 + K2*H2

R2         (  15.00 +  10.00 )* .9740 +  50.00*(    .20)* .02597
---- = ----------------------------------------------------------------------
R1       (  15.00 +  10.00 )* .9740 +  50.00* .02597 +  .002* .0550 * 365000

                              R2
                             ---- =   .2020
                              R1


    TOTAL APPARENT REMOVAL RATE.....

                        KT = K1 + BETA*R2/R1*(K2+KS)    /DAY

               .0046 =   .00302 + 2.6986* .202*(  .00250 +  .00049)
```

```
                    TIME VARIABLE BEHAVIOR
                    ----------------------


                 TIME     CT1(T)/CT1(SS)     CT2(T)/CT2(SS)
                (DAYS)         (%)                (%)
                 29.17        25.00              21.95
                 72.45        50.00              47.97
                170.27        80.00              79.19
                244.27        90.00              89.59




                DIAGNOSIS
                ---------

MAGNITUDES:  WATER COLUMN REACTION AND TRANSPORT     (/DAY)
     K1 =            .00302      WA*FP1/H1 =    .00327
     KL*FD1/H1 =     .12744
----   S1 = K1 + WA*FP1/H1 + KL*FD1/H1 =  .13373



MAGNITUDES:  SEDIMENT LAYER REACTION AND TRANSPORT     (/DAY)
     K2 =            .00250      WS*FP2/H2 =     .00049
     KL*FD2/H2 =     .23613      WRS*FP2/H2 =    .00073
----   S2 = K2 + WS*FP2/H2 + KL*FD2/H2 + WRS*FP2/H2 =  .23984


ST = S1 + S2 =  .37357     ST + 1/T0 =  .37357 +  .00997 =  .38354


EXPONENTS:      (/DAY)
     G1 (EXACT) =    .37417
     G1 (APPROX) = ST + 1/T0 =    .38354
     G2 (EXACT) =    .00937
     G2 (APPROX) = S2/(ST + 1/T0) * (KT + 1/T0) =    .00914
```

```
$storage:2
$debug
C**********           SIMPLIFIED STREAM/LAKE ANALYSIS PROGRAM          ***********
C
      REAL  TITLE(20),CHEMNA(10),KA,KS,KRS,KL,KLP,KL1,KL2,M1,M2,KT,K1,K2
     .      ,PIE(2),KHYDR(2),KBIOL(2),KVOLA,KOXID(2),KTOT(2),KPHOT
     .      ,WTOT(2),TSS(4),CT1SS(4),CT2SS(4),PERCNT(4),LOG10,MANTIS
     .     ,DTG(2),TENDG(2)
      CHARACTER*4   LAKE,STREAM,WBODY
      CHARACTER*30 CNAME
      CHARACTER*30 PNAME
       EQUIVALENCE   (PIE(1),PIE1) , (PIE(2),PIE2)
     .   ,  (KTOT(1),K1) , (KTOT(2),K2)
      INTEGER OUT
      DATA   LAKE/'LAKE'/,STREAM/'STRE'/
      DATA   PERCNT/0.75,0.5,0.2,0.1/ , TSS/4*1./
      DO 33 I=1,24
      WRITE (0,34)
   34 FORMAT(/)
   33 CONTINUE
      WRITE (0,35)
   35 FORMAT(//////T10,'SIMPLIFIED STREAM/LAKE ANALYSIS PROGRAM',
     .   ///T5,'ENTER NAME OF INPUT FILE (i.e. SLSA.INP) - ->'\)
      READ (0,36) CNAME
   36 FORMAT(A30)
      WRITE (0,37)
   37 FORMAT(///T5,'ENTER NAME OF OUTPUT FILE (i.e SLSA.OUT) - ->'\)
      READ (0,36) PNAME
C
      DATA   IN/1/,OUT/2/
      OPEN(1,FILE =CNAME,STATUS='OLD',ACCESS='SEQUENTIAL')
      OPEN(2,FILE =PNAME,ACCESS='SEQUENTIAL')
C
      READ(IN,1000)  TITLE
 1000 FORMAT(20A4)
      WRITE(OUT,1050)  TITLE
 1050 FORMAT(///31X,'S L S A'/30X,9('-')//
     .   5X,'DEVELOPED BY HYDROQUAL,  INC.'/
     .   5X,'                MAHWAH,  NJ 07430'/
     .   5X,'                201-529-5151'//
     .   5X,'REFERENCE:  DITORO,D.M., O'CONNOR,D.J., THOMANN,R.V.'/
     .   5X,'"MODELING THE FATE OF CHEMICALS IN THE AQUATIC'/
     .   5X,'ENVIRONMENT", T. EDITED BY DICKSON,K.L., MAKI,A.W.,'/
     .   5X,'CAIRNS,J., ANN ARBOR SCIENCE, 1982, CHAPTER 10,'/
     .   5X,'PG. 165-189.'//5X,20A4//)
C        READ WATER BODY TYPE
      READ(IN,1000)  WBODY
      IF(WBODY.NE.LAKE .AND. WBODY.NE.STREAM)  GO TO 900
      IF(WBODY.EQ.LAKE)   WRITE(OUT,2000)
      IF(WBODY.EQ.STREAM)   WRITE(OUT,2050)
 2000 FORMAT(20X,'SIMPLE LAKE ANALYSIS'/)
 2050 FORMAT(29X,'SIMPLE STREAM ANALYSIS'/)
C        READ PHYSICAL PARAMETERS
      IF(WBODY.EQ.LAKE)   READ(IN,2100)   Q,VORA,WK,H1,H2,
     .   M1,M2,KL,WRS,WS
      IF(WBODY.EQ.STREAM)   READ(IN,2100)   Q,VORA,
     .   WK,H1,H2,M1,M2,KL,WRS,WS,XTOT,DELTAX
 2100 FORMAT(8F10.0)
C        SOLIDS BALANCE YIELDS SETTLING VELOCITY
      WA = M2*(WS+WRS)/M1/1000./365.
```

```
      WRITE(OUT,2150)  Q,WK
 2150 FORMAT(20X,'PHYSICAL PARAMETERS'/20X,19('-')/20X,'FLOW',13('.'),
     .   1P,E10.3,' M**3/SEC'/20X,'LOAD',13('.'),E10.3,' KG/DAY')
      IF(WBODY.EQ.STREAM)    GO TO 60
      TO = VORA/Q/86400.
      TO1 = 1./TO
      WRITE(OUT,2160)   VORA,TO
 2160 FORMAT(1P,20X,'VOLUME',11('.'),E10.3,' M**3'/20X,'DETENTION TIME..
     ..',E10.3,' DAYS')
      GO TO 70
   60 WRITE(OUT,2180)   VORA
 2180 FORMAT(1P,20X,'X-SECT AREA',6('.'),E10.3,' M**2')
   70 WRITE(OUT,2200)   H1,H2,M1,M2,WA,WS,WRS,KL
 2200 FORMAT(//1X,'WATER COLUMN',28X,
     .   'SEDIMENT LAYER'/1X,12('-'),28X,14('-')/1X,
     .  2('DEPTH............',F10.2,' METERS',6X)/1X,
     .  2('SUSP SOLIDS......',F10.0,' MG/L',8X)/1X,'SETTLING VEL.....'
     .   ,F10.3,' M/DAY',7X,'SEDIMENT VEL.....',F10.1,' MM/YR'//1X,
     .   'RESUSP VEL.......',F10.1,' MM/YR'/1X,'DIFF EXCH COEFF..',
     .   F10.1,' CM/DAY')
   80 READ(IN,2300,END=900)   CHEMNA,PIE,KHYDR,KOXID,KBIOL,KPHOT,
     .    KVOLA
 2300 FORMAT(10A4,4F10.0/(8F10.0))
      KTOT(1) = KHYDR(1) + KOXID(1) + KBIOL(1) + KPHOT + KVOLA
      KTOT(2) = KHYDR(2) + KOXID(2) + KBIOL(2)
      Z1 = M1*PIE1*1.E-06
      FD1 = 1./(1.+Z1)
      FP1 = Z1*FD1
      Z2= M2*PIE2*1.E-06
      FD2 = 1./(1.+Z2)
      FP2 = Z2*FD2
      WRITE(OUT,2400)   CHEMNA,(J,PIE(J),J=1,2),FP1,FP2,FD1,FD2
 2400 FORMAT(//20X,'CHEMICAL/PHYSICAL PARAMETERS'/20X,28('-')/16X,'FOR '
     .   ,10A4/20X,'WATER COLUMN',28X,'SEDIMENT LAYER'/20X,12('-'),28X,
     .   14('-')/20X,2('PARTITION COEFF',25X)/
     .   1X,2('(P',I1,')............',1P,E10.3,' L/KG',8X)//
     .   1X,2('PHASE FRACTIONS',25X)/
     .   1X,2('PARTICULATE......',0P,F10.5,13X)/
     .   1X,2('DISSOLVED........',F10.5,13X)//)
      WRITE(OUT,2500)   KHYDR,KOXID,KBIOL,KPHOT,KVOLA,(J,KTOT(J),J=1,2)
 2500 FORMAT(1X,2('HYDROLYSIS RATE..',F10.5,' /DAY',8X)/
     .   1X,2('OXIDATION RATE...',F10.5,' /DAY',8X)/
     .   1X,2('BIOLYSIS RATE....',F10.5,' /DAY',8X)/
     .   1X,'PHOTOLYSIS RATE..',F10.5,' /DAY',8X/
     .   1X,'VOLATILITY RATE..',F10.5,' /DAY',8X//
     .   1X,2('TOTAL REMOVAL',27X)/
     .   1X,2('RATE (K',I1,')........',F10.5,' /DAY',8X))
C
C         DIAGNOSIS
C
      WAP = WA*1000.*365.
      KA = WA*FP1/H1
      KS = WS*FP2/H2/1000./365.
      KRS = WRS*FP2/H2/1000./365.
      KLP = 10.*365.*KL
      KL1 = KL*FD1/H1/100.
      KL2 = KL*FD2/H2/100.
      WTOT(1) = KTOT(1)*H1
      WTOT(2) = KTOT(2)*H2
      BETA = (M2*H2*FP1)/(M1*H1*FP2)
```

```
      PRATIO = PIE2/PIE1
      R2 = (KRS + KS) + KL2*PRATIO
      R1 = (KRS + KS) + KL2 + KTOT(2)
      R2R1 = R2/R1
      KT = KTOT(1) + BETA*R2R1*(KTOT(2)+KS)
      IF(WBODY.EQ.LAKE)  CT1 = (WK/Q) * 11.57407 * (1./(1.+TO*KT))
      IF(WBODY.EQ.STREAM)   CT1 = WK/Q/0.0864
      CT2 = BETA*R2R1*H1/H2*CT1
      WRITE(OUT,3400)   CHAR(12),CT1,CT2,FD1,FD2,FP1,FP2
 3400 FORMAT(1X,A1,//35X,1P,'STEADY STATE SOLUTION'/35X,21('-')//
     .   /25X,'CT1 =',E10.3,' UG/L',5X,'CT2 =',E10.3,' UG/L'/
     .   25X,'FD1 =',0P,F9.5,11X,'FD2 =',F9.5/
     .   25X,'FP1 =',F9.5,11X,'FP2 =',F9.5/)
      WRITE(OUT,3000)   WAP,WS,KS,WRS,KLP,(KTOT(I),I=1,2)
 3000 FORMAT(//40X,'DIAGNOSIS'/40X,9('-')//
     .   45X,'VELOCITIES                  RATES'/50X,'MM/YR',15X,'/DAY'/
     .   14X,'WATER COLUMN SETTLING......    (WA)',F8.0/
     .   14X,'SEDIMENTATION..............    (WS)',F8.0,8X,'(KS)',F8.5/
     .   14X,'RESUSPENSION...............   (WRS)',F8.0/
     .   14X,'DIFFUSIVE EXCH COEFF.......    (KL)',F8.0/
     .   14X,'WATER COLUMN REMOVAL.......',23X,'(K1)',F8.5/
     .   14X,'SEDIMENT LAYER REMOVAL.....',23X,'(K2)',F8.5///)
      WRITE(OUT,3100)   BETA
 3100 FORMAT(14X,'SEDIMENT CAPACITY FACTOR.....'//
     .   38X,'M2*H2*FP1'/30X,'BETA = ----------- =',F9.3/38X
     .   ,'M1*H1*FP2'///)
      WRITE(OUT,3200)   WRS,WS,FP2,KL,PRATIO,FD2,WRS,WS,FP2,KL,FD2,
     .   KTOT(2),H2,R2R1
 3200 FORMAT(14X,'RATIO OF PARTICULATE CONCENTRATIONS.....'//
     .   26X,'R2',5X,'(WRS+WS)*FP2 + KL*(P2/P1)*FD2'/25X,4('-'),
     .   ' = ',31('-')/26X,'R1',5X,'(WRS+WS)*FP2 + KL*FD2 + K2*H2'//
     .   4X,'R2',8X,'(',F7.2,' +',F7.2,' )*',F6.4,' +',F7.2,'*(',F6.2,
     .   ')*',F7.5/3X,4('-'),' = ',70('-')/4X,'R1',5X,'(',F7.2,' +',
     .   F7.2,' )*',F6.4,' +',F7.2,'*',F7.5,' +',F6.3,'*',F6.4,' *',
     .   ' 365000'//37X,'R2'/36X,4('-'),' = ',F7.4/37X,'R1'///)
      WRITE(OUT,3300)   KT,KTOT(1),BETA,R2R1,KTOT(2),KS
 3300 FORMAT(14X,'TOTAL APPARENT REMOVAL RATE.....'//
     .   30X,'KT = K1 + BETA*R2/R1*(K2+KS)    /DAY'//17X,F10.4,' = ',
     .   F8.5,' +',F7.4,'*',F5.3,'*(',F8.5,' +',F8.5,')')
      IF(WBODY.EQ.STREAM)   GO TO 200
      S1 = K1 + KA + KL1
      S2 = K2 + KRS + KS + KL2
      S1P = S1 + 1./TO
      ST = S1 + S2
      STP = ST + 1./TO
C         EXPONENTS
      Z0 = (K1+TO1)*S2 + (KS+K2)*(S1-K1)
      Z0 = SQRT(1.-4.*Z0/(S1P+S2)**2)
      G2 = (S1P+S2)/2.*(1.-Z0)
      G1 = (S1P+S2)/2.*(1.+Z0)
C         COEFFICIENTS
      C1 = (S2-G2)/(G2-G1)/G2/TO
      C2 = (S2-G1)/(G1-G2)/G1/TO
      G1APP = S2*(1.+BETA*R2R1) + K1+TO1
      G2APP = S2/(ST+TO1)*(KT+TO1)
      C0 = 1./(1.+TO*KT)
      TRM1 = C1/C0
      TRM2 = C2/C0
      DO 100 I=1,4
   90 E1 = TRM1*EXP(-G2*TSS(I))
```

```
      E2 = TRM2*EXP(-AMIN1(G1*TSS(I),50.))
      F9 = PERCNT(I) + E1 + E2
      F8 = -(G2*E1 + G1*E2)
      T8 = TSS(I) - F9/F8
      IF(ABS(T8-TSS(I)).LT.1.0E-06*TSS(I))   GO TO 100
      TSS(I) = T8
      GO TO 90
  100 CONTINUE
C         COMPUTE CT2(T)/CT2(SS) AT TSS
      DO 120 I=1,4
      E1 = EXP(-G2*TSS(I))
      E2 = EXP(-AMIN1(G1*TSS(I),50.))
      Z2 = 1. + G1/(G2-G1)*E1 + G2/(G1-G2)*E2
      Z1 = 1. + G1*(S2-G2)/(S2*(G2-G1))*E1 + G2*(S2-G1)/(S2*(G1-G2))*E2
C         ADD 0.001 FOR COMPUTER ROUND-OFF
      CT1SS(I) = 100.*Z1 + 0.001
  120 CT2SS(I) = 100.*Z2
      WRITE(OUT,4100)  CHAR(12),(TSS(I),CT1SS(I),CT2SS(I),I=1,4)
 4100 FORMAT(1X,A1,//30X,'TIME VARIABLE BEHAVIOR'/30X,22('-')///
     .    22X,'TIME    CT1(T)/CT1(SS)    CT2(T)/CT2(SS)'/
     .    21X,'(DAYS)',2(8X,'(%)',7X)/(17X,F9.2,F13.2,8X,F10.2))
      WRITE(OUT,3500)  K1,KA,KL1,S1
 3500 FORMAT(////20X,'DIAGNOSIS'/20X,9('-')//
     .    5X,'MAGNITUDES:  WATER COLUMN REACTION AND TRANSPORT',5X,
     .    '(/DAY)'/10X,'K1 =',8X,F8.5,6X,'WA*FP1/H1 = ',F8.5/
     .    10X,'KL*FD1/H1 = ',F8.5/
     .    5X,'----   S1 = K1 + WA*FP1/H1 + KL*FD1/H1 =',F8.5///)
      WRITE(OUT,3600)   K2,KS,KL2,KRS,S2,ST,ST,T01,STP
 3600 FORMAT(5X,'MAGNITUDES:  SEDIMENT LAYER REACTION AND TRANSPORT'
     .    5X,'(/DAY)'/10X,'K2 =',8X,F8.5,6X,'WS*FP2/H2 = ',F9.5/
     .    10X,'KL*FD2/H2 = ',F8.5,6X,'WRS*FP2/H2 = ',F8.5/
     .    5X,'----   S2 = K2 + WS*FP2/H2 + KL*FD2/H2 + WRS*FP2/H2 =',
     .    F8.5///5X,'ST = S1 + S2 =',F8.5,5X,
     .    'ST + 1/T0 =',F8.5,' +',F8.5,' =',F8.5///)
      WRITE(OUT,3800)   G1,G1APP,G2,G2APP
 3800 FORMAT(5X,'EXPONENTS:      (/DAY)'/
     .    10X,'G1 (EXACT) =',F9.5/
     .    10X,'G1 (APPROX) = ST + 1/T0 =',F9.5/
     .    10X,'G2 (EXACT) =',F9.5/
     .    10X,'G2 (APPROX) = S2/(ST + 1/T0) * (KT + 1/T0) =',F9.5/)
      DO 140 I=1,2
      IF(I.EQ.1)  RECIP = 1./G1
      IF(I.EQ.2)  RECIP = 1./G2
      TENDG(I) = 4.*RECIP
      LOG10 = ALOG10(TENDG(I))
      MANTIS = LOG10 - IFIX(LOG10)
      EXPON = IFIX(LOG10) - 1.
      DO 130 J=1,10
      IF(MANTIS.LT.ALOG10(FLOAT(J)))   GO TO 140
  130 CONTINUE
  140 DTG(I) = FLOAT(J-1)*10.**EXPON
      I=1
      IT = 1
      DT = DTG(1)
      TEND = TENDG(1)
      TIME = DT
      WRITE(OUT,3850) CHAR(12)
 3850 FORMAT(1X,A1,//5X,'TIME',5X,3('-  '),'W A T E R   C O L U M N  ',
     .    3('-  ')/4X,'(DAYS)',23X,'(UG/L)'/
     .    7X,(10X,'TOTAL',9X,'DISSOLVED',4X,'PARTICULATE')/)
```

```
      CT01 = 11.57407*(WK/Q/T0) * S2/G1/G2
      CT02 = 11.57407*(WK/Q/T0)*(KA*H1/H2 + KL2*FD1/FD2) /G1/G2
  150 E1 = EXP(-G2*TIME)
      E2 = EXP(-AMIN1(G1*TIME,50.))
      Z2 = 1. + G1/(G2-G1)*E1 + G2/(G1-G2)*E2
      Z1 = 1. + G1*(S2-G2)/(S2*(G2-G1))*E1 + G2*(S2-G1)/(S2*(G1-G2))*E2
      CT1 = CT01*Z1
      CT1D = FD1*CT1
      CT1P = FP1*CT1
      CT2 = CT02*Z2
      CT2D = FD2*CT2
      CT2P = FP2*CT2
      WRITE(OUT,3875)   TIME,CT1,CT1D,CT1P
 3875 FORMAT(1P,3X,F7.1,3E15.4)
      IT = IT + 1
      TIME = FLOAT(IT)*DT + 0.0001*DT
      IF(TIME.LT.TEND)   GO TO 150
      I = I + 1
      IF(I.GT.2)   GO TO 152
      DT = DTG(2)
      IT = TIME/DT
      TEND = TENDG(2)
      GO TO 150
  152 CONTINUE
      I=1
      IT = 1
      DT = DTG(1)
      TEND = TENDG(1)
      TIME = DT
      WRITE(OUT,3851)
 3851 FORMAT(///5X,'TIME',3X,3('-  '),'S E D I M E N T   L A Y E R ',
     .    3('-  ')/4X,'(DAYS)',23X,'(UG/L)'/
     .    7X,(10X,'TOTAL',9X,'DISSOLVED',4X,'PARTICULATE')/)
      CT01 = 11.57407*(WK/Q/T0) * S2/G1/G2
      CT02 = 11.57407*(WK/Q/T0)*(KA*H1/H2 + KL2*FD1/FD2) /G1/G2
  151 E1 = EXP(-G2*TIME)
      E2 = EXP(-AMIN1(G1*TIME,50.))
      Z2 = 1. + G1/(G2-G1)*E1 + G2/(G1-G2)*E2
      Z1 = 1. + G1*(S2-G2)/(S2*(G2-G1))*E1 + G2*(S2-G1)/(S2*(G1-G2))*E2
      CT1 = CT01*Z1
      CT1D = FD1*CT1
      CT1P = FP1*CT1
      CT2 = CT02*Z2
      CT2D = FD2*CT2
      CT2P = FP2*CT2
      WRITE(OUT,3875)   TIME,CT2,CT2D,CT2P
      IT = IT + 1
      TIME = FLOAT(IT)*DT + 0.0001*DT
      IF(TIME.LT.TEND)   GO TO 151
      I = I + 1
C         CHECK IF FINISHED TIME VARIABLE RESPONSE
C         IF SO GO BACK AND GET NEW CHEMICAL
      IF(I.GT.2)   GO TO 80
      DT = DTG(2)
      IT = TIME/DT
      TEND = TENDG(2)
      GO TO 151
      CALL EXIT
C         STREAM SOLUTION
  200 C5 = WK/Q/0.0864
```

```
      U5 = Q*86.4/VORA
      S9 = BETA*R2R1*H1/H2
      S1 = K1 + KA + KL1
      ISTEP = XTOT/DELTAX+2
      WRITE(OUT,3900) CHAR(12)
 3900 FORMAT(1X,A1,///12X,'RECEIVING WATER RESPONSE'//
     .   12X,'DISTANCE     CT2         CT1 '/
     .   14X,'(KM)',5X,'(UG/L)',5X,'(UG/L)'//)
      DO 250 I=1,ISTEP
      X = FLOAT(I-1)*DELTAX
      IF(X.GT.XTOT)   X = XTOT
      E1 = EXP(-KT*X/U5)
      CT1 = C5*E1
      CT2 = S9*CT1
  250 WRITE(OUT,4000)  X,CT2,CT1
 4000 FORMAT(8X,F10.2,2F11.2,)
C        FINISHED STREAM RESPONSE, GO BACK FOR NEW CHEMICAL
      GO TO 80
  900 CALL EXIT
      END
```

Modeling the Fate of Chemicals In the Aquatic Environment

Edited by

Kenneth L. Dickson
Alan W. Maki
John Cairns, Jr.

ANN ARBOR SCIENCE
THE BUTTERWORTH GROUP , 1982

CHAPTER 10

SIMPLIFIED MODEL OF THE FATE OF PARTITIONING CHEMICALS IN LAKES AND STREAMS

Dominic M. Di Toro, Donald J. O'Connor and Robert V. Thomann
HydroQual, Inc.
Mahwah, New Jersey 07430
and Environmental Engineering and Science Program
Manhattan College
Bronx, NY 10471

John P. St. John
HydroQual, Inc.
Mahwah, New Jersey 07430

This chapter addresses the problem of analyzing the fate of chemicals discharged into receiving waters, specifically lakes and streams. The focus is on contemporary industrial chemicals and the mechanisms that affect their distribution in the aquatic environment. These chemicals are associated, to a greater or lesser degree, with suspended and sedimented particles that are present in all receiving waters. Thus, particle transport mechanisms markedly affect the chemical's fate. The analysis that has been developed includes these mechanisms as an integral part of the formulation, as well as the other kinetic, transfer and transport processes of importance. It is similar in many ways to previously developed models [1-6]; however, the focus of this effort is to analyze exhaustively the solutions, so that an intuitive grasp of the problem can be developed.

The methodology is based on the principle of conservation of mass. It is expressed in mathematical form for application to lakes, impoundments and flowing streams. The solutions have been analyzed in detail and cast into forms that are suitable for desktop calculations. The results are comprehensible without elaborate numerical computer-based calculations. Thus, they provide direct insight into the relative importance of the various mechanisms that determine the fate of a particular chemical in a specific body of water.

DEFINITIONS, MECHANISMS AND MASS-BALANCE EQUATIONS

The receiving water models for lakes and streams include the mechanisms illustrated in Figure 1 and defined in Table I. The loading rate of chemical W_T is the primary input to the water column. The relevant reactions that remove or transform the chemical are: hydrolysis, oxidation, biodegradation, photolysis and volatilization. These are summed to yield the total degradation rates in the water column K_1 and sediment K_2. The adsorption/desorption reaction is assumed to be at equilibrium, and the fraction of the chemical mass that is either dissolved or adsorbed to particulates is determined by the mass of adsorbing solids m and the partition coefficients π in the water column (m_1 and π_1) and the sediment (m_2 and π_2), respectively.

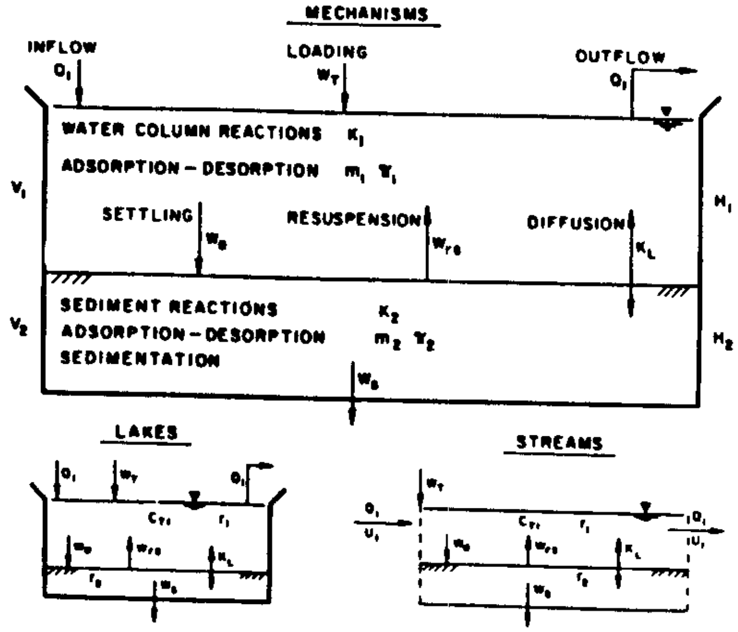


Figure 1. Receiving water volume segment: mechanisms and application to lakes and streams.

Table I. Definitions

Parameter	Water Column	Sediment
Chemical/Biological		
Loading rate (kg/day)	W_T	
Sum of hydrolysis, oxidation biodegradation, photolysis and volatilization rates (/day)	K_1	K_2
Partition coefficients (liter/kg)	π_1	π_2
Physical		
Solids concentration (mg/l)	m_1	m_2
Depths (m)	H_1	H_2
Volumes (m^3)	V_1	V_2
Flowrate (m^3/day)	Q_1	
Velocity (m/day)	$U_1 = Q_1H_1/V_1$	
Detention time (days)	$t_{01} = V_1/Q_1$	
Settling velocity (m/day)	w_s	
Resuspension velocity (mm/yr)		w_{rs}
Diffusion exchange coefficient (cm/day)		K_L
Sedimentation		
Velocity (mm/yr)		w_s
Rate coefficient (/day)		$K_s = w_s/H_2$
Concentrations		
Total dissolved + particulate (μg/l)	c_{T1}	c_{T2}
Particulate (μg chemical/g solids)	r_1	r_2
Fractions[a]		
Particulate $f_p = m\pi/(1 + m\pi)$	f_{p1}	f_{p2}
Dissolved $f_d = 1/(1 + m\pi)$	f_{d1}	f_{d2}

[a] For π in units of liter/kg and m in units of mg/l, a conversion factor of 10^{-6} kg/mg is necessary, so that these fractions are dimensionless, i.e., m (mg/l) × π(liter/kg) × 10^{-6} (kg/mg).

The geometry of the receiving water segment is specified by the depths of the water column H_1, and the active sediment layer H_2, together with the volumes of these segments V_1 and V_2, respectively. The aqueous transport is specified by the flowrate of the water column Q_1 and the velocity U_1, in streams, or the hydraulic detention time t_{01}, in lakes.

The sediment/water column transport of particulates is specified by the settling velocity of adsorbing particles to the sediment layer w_s and their resuspension velocity from the sediment w_{rs}. Dissolved-phase transport is specified by the diffusive exchange coefficient K_L, which is a function of the interstitial and overlying water diffusion coefficients.

The mass-balance equation for total chemical concentration in the water column (c_{T1}) and sediment (c_{T2}) segments are constructed from the sum of all the rates of change produced by each of these mechanisms. The mass-balance equation for the water column is shown by:

$$\frac{dc_{T1}}{dt} = \left.\frac{dc_{T1}}{dt}\right|_{\text{kinetic}} + \left.\frac{dc_{T1}}{dt}\right|_{\text{outflow}} + \left.\frac{dc_{T1}}{dt}\right|_{\text{diffusion}} + \left.\frac{dc_{T1}}{dt}\right|_{\text{particle}} + \left.\frac{dc_{T1}}{dt}\right|_{\text{discharge}} \tag{1}$$

The mass-balance equation for the sediment is:

$$\frac{dc_{T2}}{dt} = \left.\frac{dc_{T2}}{dt}\right|_{\text{kinetic}} + \left.\frac{dc_{T2}}{dt}\right|_{\text{diffusion}} + \left.\frac{dc_{T2}}{dt}\right|_{\text{particle}} \tag{2}$$

The water column kinetic derivative is expressed in terms of the sum of all water column decay rates K_1, which is computed as the sum of the dissolved hydrolysis, oxidation, biodegradation, photolysis and volatilization rates, multiplied by the fraction of total chemical that is dissolved f_{d1}; plus the analogous particulate rates multiplied by the particulate fraction f_{p1}. The sediment decay rate K_2 is computed in similar fashion using f_{d2} and f_{p2}. The reactions are all assumed to be first-order in the chemical concentration; they may also be functions of pH (hydrolysis) or microbial biomass (biodegradation), but that does not affect the mass-balance equations.

The outflow term is expressed in terms of the volumetric outflow rate in the water column (Q_1). The diffusive exchange of dissolved chemical between the overlying water column and the interstitial water of the sediment is expressed in terms of a mass transfer coefficient K_L (cm/day), which can be shown to be the ratio of interstitial water diffusion coefficient and the characteristic length of the gradient of dissolved chemical [7]. It multiplies the gradient of dissolved chemical concentration to produce the diffusion flux. The particle-exchange term in the water column is the difference between the loss via settling (with velocity w_a) of particulate chemical $f_{p1}c_{T1}$ and the gain via particle resuspension of sediment particulate chemical, $f_{p2}c_{T2}$ (with velocity w_{rs}). The analogous expressions in the sediment equations are the negative of the water column expressions, since a loss from the water column is a gain for the sediment layer and vice versa. The division by the depths of each layer properly accounts for the differing volumes of these two layers. Finally, the loss of sediment particulate chemical via burial is expressed in terms of a sedimentation velocity (w_s), which accounts for particles leaving the active sediment layer as sediment depth increases via sedimentation. Substituting the appropriate expressions into Equations 1 and 2 yields:

$$\frac{dc_{T1}}{dt} = -K_1c_{T1} - \frac{Q_1}{V_1}c_{T1} - \frac{K_L}{H_1}(f_{d1}c_{T1} - f_{d2}c_{T2}) - \frac{w_a}{H_1}f_{p1}c_{T1} + \frac{w_{rs}}{H_1}f_{p2}c_{T2} + \frac{W_T}{V_1} \tag{3}$$

$$\frac{dc_{T2}}{dt} = -K_2c_{T2} + \frac{K_L}{H_2}(f_{d1}c_{T1} - f_{d2}c_{T2}) + \frac{w_a}{H_2}f_{p1}c_{T1} - \frac{w_{rs}}{H_2}f_{p2}c_{T2} - \frac{w_s}{H_2}f_{p2}c_{T2} \tag{4}$$

These two differential equations specify the mass-balance relationships that are implied by the mechanisms of degradation, outflow, interstitial and water column diffusion, particle transport, and chemical mass discharge to the receiving water segment. It remains to solve these equations and interpret the results.

STEADY-STATE SOLUTION

The differential equations for c_{T1} and c_{T2} specify the response of the water column and sediment segment concentrations to a constant chemical discharge of magnitude W_T. The time-variable behavior has been investigated elsewhere [7]. In this chapter, solutions for the steady-state concentrations are presented and discussed.

For steady-state conditions, $dc_{T1}/dt = 0$ and $dc_{T2}/dt = 0$, and what remains are two simultaneous linear algebraic equations that can be solved directly. The results are given in Table II. Although these expressions do indeed give the solution to the steady-state behavior of the receiving-water segment, they provide no insight at all into the behavior of the solution as a function of the physical, transport and chemical parameters that describe the receiving-water segment. This is a very uncomfortable situation for the analyst, since he is essentially in the dark concerning the influence of each parameter on the predicted behavior of

Table II. Receiving Water Segment Equations and Solutions

Simultaneous Equations

$$\left(\frac{Q_1}{V_1} + K_1 + \frac{w_a}{H_1} f_{p1} + \frac{K_L}{H_1} f_{d1}\right) c_{T1} - \left(\frac{w_{rs}}{H_1} f_{p2} + \frac{K_L}{H_1} f_{d2}\right) c_{T2} = \frac{W_T}{V_1}$$

$$\left(\frac{w_a}{H_2} f_{p1} + \frac{K_L}{H_2} f_{d1}\right) c_{T1} - \left(K_2 + \frac{w_{rs}}{H_2} f_{p2} + \frac{K_L}{H_2} f_{d2} + \frac{w_s}{H_2} f_{p2}\right) c_{T2} = 0$$

Solutions:

$$c_{T1} = \frac{\frac{W_T}{V_1}\left(\frac{w_{rs}}{H_2} f_{p2} + \frac{w_s}{H_2} f_{p2} + \frac{K_L}{H_2} f_{d2} + K_2\right)}{\left(\frac{Q_1}{V_1} + K_1 + \frac{w_a}{H_1} f_{d1} + \frac{K_L}{H_1} f_{d1}\right)\left(\frac{w_{rs}}{H_2} f_{p2} + \frac{w_s}{H_2} f_{p2} + \frac{K_L}{H_2} f_{d2} + K_2\right) - \left(\frac{w_{rs}}{H_1} f_{p2} + \frac{K_L}{H_1} f_{d2}\right)\left(\frac{w_a}{H_2} f_{d1} + \frac{K_L}{H_2} f_{d1}\right)}$$

$$c_{T2} = \frac{c_{T1}\left(\frac{w_a}{H_2} f_{p1} + \frac{K_L}{H_2} f_{d1}\right)}{K_2 + \frac{w_{rs}}{H_2} f_{p2} + \frac{K_L}{H_2} f_{d2} + \frac{w_s}{H_2} f_{p2}}$$

and

$c_{d1} = f_{d1} c_{T1}$; $c_{p1} = f_{p1} c_{T1}$

$c_{d2} = f_{d2} c_{T2}$; $c_{p2} = f_{p2} c_{T2}$

the fate of the chemical. Of course it is possible to vary each parameter systematically and to observe the variation of the predicted solution, but there is no substitute for the insight that can be gained from a properly simplified solution.

It is possible to cast the solution into a form that conveys an intuitive understanding of its properties. The algebraic details are given elsewhere [7]. To understand the motivation that leads to the final form of the results, consider the following simple situation. A discharge of magnitude W_T enters the water column segment of volume V_1 with outflow Q_1, and therefore hydraulic detention time $t_{01} = V_1/Q_1$. The chemical undergoes no interaction with the suspended particles present and does not interact in any way with the sediment. It is only subject to water column decay, with first-order rate constant K_1. The solution for this case is well known to be:

$$c_{T1} = \frac{W_T/Q_1}{1 + K_1 t_{01}} \tag{5}$$

and its behavior is evident by inspection.

The surprising result is that the solution for the general case, given in Table II can be cast into exactly this form:

$$c_{T1} = \frac{W_T/Q_1}{1 + K_T t_{01}} \tag{6}$$

where the apparent total removal rate K_T is given by the equation:

$$K_T = K_1 + \beta \frac{r_2}{r_1} (K_2 + K_s) \tag{7}$$

The apparent total removal rate K_T is seen to be the sum of two expressions: K_1 (the total water column decay rate) and $\beta r_2/r_1\ (K_2 + K_s)$. This latter expression has three terms, each of which have intuitive meanings. $K_2 + K_s$ is the sum of the total sediment decay rate (K_2) and the decay rate due to loss by sedimentation:

$$K_s = \frac{w_s}{H_2} f_{p2} \tag{8}$$

These are the only mechanisms that actually remove the chemical from the sediment. Therefore, it is not surprising that they play a major role in determining the apparent total removal rate. However, their effect is modified by the remaining terms.

The parameter β:

$$\beta = \frac{m_2 H_2 f_{p1}}{m_1 H_1 f_{p2}} \qquad (9)$$

is essentially the ratio of the total mass of solids in the sediment segment $m_2 AH_2 = m_2 V_2$ to that in the water column $m_1 AH_1 = m_1 V_1$, where A is the interfacial surface area. It is modified by the ratio of particulate chemical in the water column f_{p1} to that in the sediment segment f_{p2}. The parameter β accounts for the relative importance of the quantity of solids and chemical in the sediment mass relative to the water column. For a small, active sediment mass relative to the water column mass of suspended solids mass, $m_2 V_2 \ll m_1 V_1$ and β (which is termed the sediment capacity factor) is small, so that the sediment has a negligible effect on the water column concentration, unless the sediment decay rates $K_2 + K_s$ are large. A more detailed analysis of the behavior of the sediment capacity factor is given below.

The ratio r_2/r_1 is the ratio of particulate chemical concentration in the sediment r_2 to that in the overlying water r_1 in units of mass of chemical per unit mass of solids. This ratio is itself determined by the solution of the steady-state equations since, by definition:

$$r_2 = f_{p2} c_{T2}/m_2 \qquad (10)$$

$$r_1 = f_{p1} c_{T1}/m_1 \qquad (11)$$

As shown elsewhere [7], r_2/r_1 is given by:

$$\frac{r_2}{r_1} = \frac{(w_{rs} + w_s) f_{p2} + K_L (\pi_2/\pi_1) f_{d2}}{(w_{rs} + w_s) f_{p2} + K_L f_{d2} + K_2 H_2} \qquad (12)$$

Although this expression is somewhat formidable, it has some very interesting properties that are immediately apparent. Remembering that this equation specifies the ratio of particulate adsorbed chemical concentrations in the sediment and overlying water, it is surprising which parameters are *not* part of the expression: the discharge rate of chemical W_T, the aqueous decay reaction rate K_1 and the hydraulic detention time t_{01}. Hence, r_2/r_1 is not dependent on these water column parameters. It is determined by the particulate transport parameters: (1) resuspension velocity w_{rs}, and sedimentation velocity w_s, each of which is modified by the particulate fraction in the sediment layer f_{p2}; (2) the diffusive exchange coefficient K_L, modified by the fraction dissolved in the sediment layer f_{d2}; (3) and the total sediment decay rate–sediment depth product $K_2 H_2$, which expresses this process as an equivalent loss velocity. These are all sediment-related parameters. (Note that the subscripts in Equation 12 all relate to the sediment segment.) The only water column parameter involved is π_1, which appears as a ratio π_2/π_1. Therefore r_2/r_1 is determined entirely by the relative magnitudes of the particulate and diffusive mass transfer coefficients, the sediment decay rate, and the partition coefficient ratio.

The reason that r_2/r_1 appears as part of the apparent total removal rate K_T (Equation 7) is that it expresses the degree of chemical contamination of the sediment particles relative to the water column particles. Since K_T is the apparent removal rate for the water column concentration c_{T1}, the ratio r_2/r_1 makes the connection between the degree of contamination in the sediment relative to that in the water column. If sediment particles are highly contaminated relative to water column particles, removal mechanisms for these particles (e.g., sedimentation K_s) have an enhanced effect on the apparent total removal rate K_T. Conversely, if r_2/r_1 is small, then removing these particles has a lesser effect on the overlying water concentration.

In fact, an alternative expression for the apparent total removal rate K_T, which clarifies this relationship, can be obtained directly from its definition (Equation 7) and those of β (Equation 9) and r_2/r_1 (Equations 10 to 12). The result is:

$$K_T = K_1 + \frac{H_2 c_{T2}}{H_1 c_{T1}} (K_2 + K_s) \qquad (13)$$

or, since volumes and depths are related via the interfacial cross-sectional area A ($V_1 = AH_1$ and AH_2), K_T can be expressed as:

$$K_T(V_1 c_{T1}) = K_1(V_1 c_{T1}) + (K_2 + K_s)(V_2 c_{T2}) \qquad (14)$$

The expression $K_T(V_1 C_{T1})$ has units mass of chemical removed/unit time. Hence the apparent total removal rate of chemical mass in the water column is the sum of the water column and sediment mass removal rates. The effectiveness of each segment's removal mechanism is in proportion to the total mass of chemical in that segment, an intuitively reasonable result.

The key to understanding the behavior of the steady-state solution is an appreciation of the mechanisms that control the sediment capacity factor (β) and the particulate concentration ratio (r_2/r_1). This is discussed in more detail below.

SEDIMENT CAPACITY RATIO

The effectiveness of sediment removal mechanisms (decay and sedimentation) as chemical sinks is determined to a large extent by the magnitude of the sediment capacity factor, β. Therefore, its variation as a function of the relevant physical and chemical parameters is an important component in the understanding of chemical fate. The capacity factor is given by the expression:

$$\beta = \frac{m_2 H_2 f_{p1}}{m_1 H_1 f_{p2}} \tag{15}$$

where m_1, m_2 = particle concentrations in the water column and sediment, respectively
H_1, H_2 = water column and sediment depths, respectively
f_{p1}, f_{p2} = particulate fractions of total chemical concentration in the water column and sediment, respectively

These latter fractions are given by:

$$f_{p1} = \frac{m_1 \pi_1}{1 + m_1 \pi_1} \tag{16}$$

$$f_{p2} = \frac{m_2 \pi_2}{1 + m_2 \pi_2} \tag{17}$$

Hence, the sediment capacity factor is a linear function of the depth ratio H_2/H_1 and a more complicated function of the water column and sediment solids concentrations m_1 and m_2, and partition coefficients π_1 and π_2.

A dimensionless plot of β vs $m_1\pi_1$ and $m_2\pi_1$ is presented in Figure 2. The depth ratio chosen for this plot is $H_1/H_2 = 1000$, corresponding for example, to a water column depth $H_1 = 10$ m and an active sediment depth $H_2 = 1$ cm. The solid contours are for $\pi_2 = \pi_1$ and the dotted contours are for $\pi_2 = 0.01\ \pi_1$, which illustrates the effect of differing partition coefficients in the water column and sediment layers that might result from sediment concentration-dependent partitioning [8]. As can be seen, this latter effect is only important for small β. The principal determinants of β are: (1) the depth ratio H_1/H_2, which is inversely proportional to β; (2) the product $m_2\pi_1$, which increases β as it increases; and (3) $m_1\pi_1$ if this product exceeds 0.1 corresponding to a dissolved column fraction f_{d1} becoming appreciably less than one. The magnitude of β can vary from 0.01 to 100 as illustrated; therefore, its value should

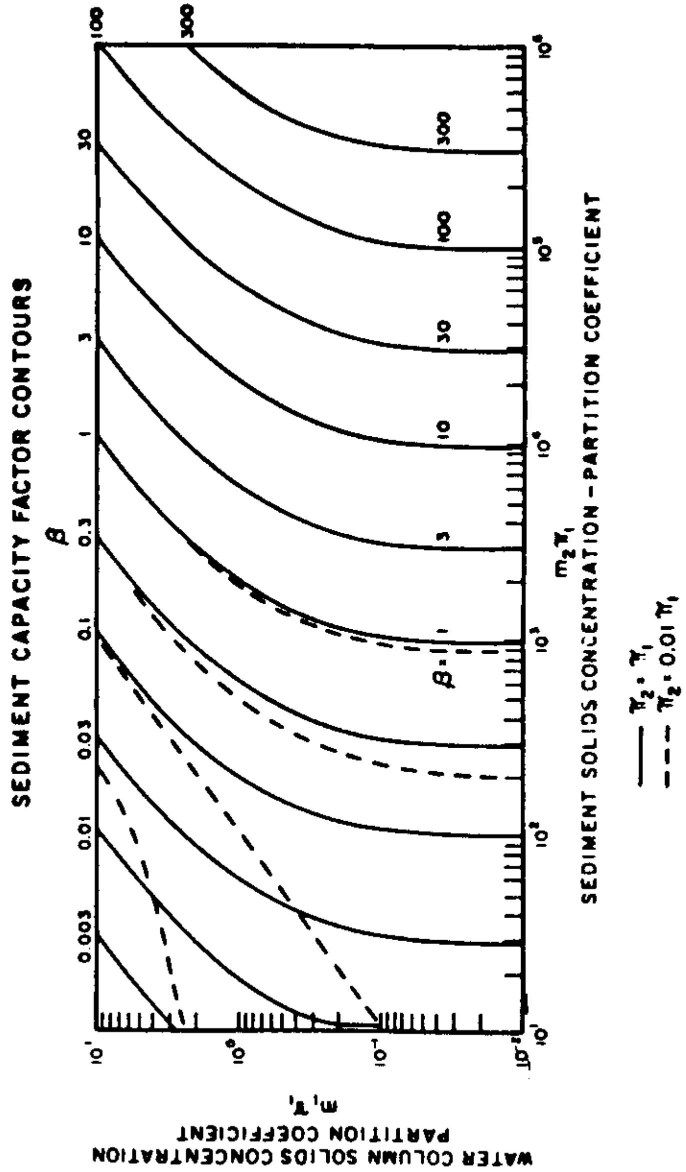


Figure 2. Contours of sediment capacity factor β vs dimensionless solids concentrations for $H_1/H_2 = 1000$.

be calculated for each situation of interest. Small values indicate that sediment-related removal mechanisms are insignificant relative to the water column concentration; large values magnify sediment effects.

PARTICULATE CONCENTRATION RATIO: THE CONDITIONS FOR EQUALITY

Certain properties of the particulate concentration ratio r_2/r_1 are apparent from inspection of its formula (Equation 12): if the resuspension and sedimentation velocity are zero, then the settling velocity is also zero; and if, in addition, the interstitial water/overlying water diffusion $K_L = 0$, then $r_2 = 0$ as expected, since these are the only mechanisms (settling and diffusion) that transport chemical to the sediment.

A more interesting question is: what conditions are necessary for $r_2 = r_1$? Conversely, what mechanisms cause the particulate concentrations to differ? The conditions for equality are:

1. Solid mass fluxes in equilibrium, that is:

$$m_1 w_a = m_2(w_{rs} + w_s) \tag{18}$$

The net flux of solids delivered to the sediment segment $m_1 w_a - m_2 w_{rs}$ is equal to the sedimentation rate $m_2 w_s$. Thus, this condition requires that there be no solids buildup in the sediment segment, which, in turn, means that there is no net storage of chemical occurring in the sediment segment because of an imbalance of solids fluxes. This condition is essentially forced by the requirement of steady state applied to the solids themselves. Hence, it should be viewed not as a restriction, but as a necessary condition implied by solids mass balance. The solids flux equality (Equation 18) is not a mathematically necessary condition. It is possible to compute r_2/r_1 without this restriction. The result is that $w_a m_1/m_2$ replaces $w_{rs} + w_s$ in the numerator of Equation 12. The effect of solids flux equality is to equate the numerator expression $w_a m_1/m_2$ to the expression $w_{rs} + w_s$.

2. The partition coefficient for sediment solids (π_2) equals the overlying water partition coefficient (π_1), or

$$\pi_2 = \pi_1 \tag{19}$$

3. There is no sediment decay:

$$K_2 = 0 \tag{20}$$

If these three conditions (solids flux equilibrium, equal partition coefficients and no sediment decay) are met, then despite the presence of settling, resuspension, sedimentation and diffusion, the particulate chemical concentrations in the water column and the sediment are equal.

This surprising result requires some explanation. The particulate concentrations are related to the dissolved concentrations via the partition coefficients: $r_2 = \pi_2 c_{d2}$. Since it is assumed that $\pi_1 = \pi_2$, the dissolved concentrations are also equal: $c_{d1} = c_{d2}$. Hence, it is not surprising that diffusion plays no role, since there is no gradient of dissolved chemical concentration between overlying water and interstitial water.

Consider the influence of particle mixing. The effect of increasing the resuspension velocity is that more particles are brought from the sediment to the water column. By the solids flux equality, the same number of particles are brought to the sediment from the water column by the increased settling velocity required by solids flux balance. These particles are transferred between segments with identical dissolved concentrations, so that they experience no change in environment and their chemical content is unchanged. Thus, there is no gradient of particulate concentration and, therefore, no driving force. Hence the increased particle mixing caused by increased resuspension and settling has no effect.

For a particulate concentration ratio $r_2/r_1 = 1$, the total apparent decay rate becomes:

$$K_T = K_1 + \beta K_s \tag{20}$$

What is remarkable about this expression is, again, which parameters are *not* involved in determining the steady-state concentrations: settling velocity, resuspension and diffusion play no role in the ultimate fate of the chemical. It is determined only by the degradation mechanisms in the water column K_1 and the loss by sedimentation and burial K_s. The effectiveness of the latter loss mechanism is determined by the magnitude of the sediment capacity factor β.

UNEQUAL PARTICULATE CONCENTRATION RATIO

If any of the conditions specified above are not met, r_2 differs from r_1. Consider the case for which the solids flux equilibrium is met. As pointed out above, this is required by the steady-state assumption. Therefore, the only mechanisms to be considered are sediment decay and unequal partitioning.

Sediment Decay

For this case, sediment decay K_2 serves to lower r_2 relative to r_1, which is reasonable, since that decay occurs only in the sediment. Consider first the case that $\pi_2 = \pi_1$. Then:

$$\frac{r_2}{r_1} = \frac{1}{1 + \dfrac{K_2 H_2}{(w_{rs} + w_s) f_{p2} + K_L f_{d2}}} \tag{21}$$

The amount by which r_2 is less than r_1 is determined by the ratio of the total sediment decay velocity $K_2 H_2$ to the sum of resuspension and sedimentation velocities, modified by the fraction particulate f_{p2} and the diffusion velocity K_L modified by the fraction dissolved f_{d2}. These velocities represent the losses of chemical from the sediment segment and suggest a definition of a total loss velocity w_{T2} as the sum of the individual velocities:

$$w_{T2} = (w_{rs} + w_s) f_{p2} + K_L f_{d2} \tag{22}$$

and an equivalent sediment detention time t_{d2} where:

$$t_{d2} = \frac{H_2}{w_{T2}} \tag{23}$$

which is analogous to the hydraulic detention time in the water column. Then the particulate ratio can be expressed as:

$$\frac{r_2}{r_1} = \frac{1}{1 + K_2 t_{d2}} \tag{24}$$

which is precisely the form of the solution to be expected in a situation with a decay rate K_2 and a detention time t_{d2}. The water column particulate concentration r_1 is analogous to the influent concentration. The resulting sediment particulate concentration is reduced relative to the influent concentration by an amount that depends on the decay rate-detention time product: $K_2 t_{d2}$. Hence, a sediment decay mechanism causes $r_2/r_1 < 1$.

Unequal Partitioning

Alternatively, consider the case for which no sediment decay occurs, $K_2 = 0$, but for which the sediment partition coefficient is less than the water column partition coefficient, or $\pi_2 < \pi_1$. This is normally the case because of the large increase of solids concentration in the sediment relative to the overlying water ($m_2 \gg m_1$) and the empirical fact that this can lower partition coefficients [8]. Then the particulate concentration ratio becomes:

$$\frac{r_2}{r_1} = \frac{1 + \gamma \pi_2/\pi_1}{1 + \gamma} \tag{25}$$

where

$$\gamma = \frac{K_L f_{d2}}{(w_{rs} + w_s) f_{p2}} \tag{26}$$

which is the ratio of diffusive to particle exchange velocities. Since $\pi_2/\pi_1 < 1$, and γ is always positive, it follows that $r_2 < r_1$. The reason is that as particles enter the sediment segment, they enter an environment where the partition coefficient is lower and they desorb a portion of their chemical burden. The result is that the dissolved concentration in the sediment segment increases relative to the overlying water:

$$\frac{c_{d2}}{c_{d1}} = \frac{\pi_1}{\pi_2}\frac{r_2}{r_1} = \frac{\dfrac{\pi_1}{\pi_2} + \gamma}{1 + \gamma} > 1 \tag{27}$$

If there is very little diffusion relative to particle mixing, then $\gamma \ll 1$ and:

$$\frac{c_{d2}}{c_{d1}} = \frac{\pi_1}{\pi_2} \qquad \gamma \ll 1 \tag{28}$$

and

$$\frac{r_2}{r_1} = 1 \qquad \gamma \ll 1 \tag{29}$$

The small amount of aqueous-phase mixing is insufficient to reduce the dissolved concentration gradient, whereas the particle mixing is sufficient to equilibrate the particle concentrations. Conversely, if there is very little particle mixing relative to diffusion mixing, then $\gamma \gg 1$:

$$\frac{r_2}{r_1} = \frac{\pi_2}{\pi_1} \qquad \gamma \gg 1 \tag{30}$$

and

$$\frac{c_{d2}}{c_{d1}} = 1 \qquad \gamma \gg 1 \tag{31}$$

In this case, the particles retain their gradient, but the dissolved mixing is sufficient to reduce the aqueous gradient.

Regardless of the magnitude of γ, it is true that

$$\frac{r_2}{r_1} < 1 \tag{32}$$

and this relationship is also true for $K_2 > 0$. Hence, it is expected that the sediment particulate concentration be less than the overlying water particulate concentration.

The only mechanism that can cause $r_2 > r_1$ is the unlikely situation that $\pi_2 > \pi_1$, or that the solids fluxes are not in balance, that is:

$$m_1 w_s > m_2(w_{rs} + w_s) \tag{33}$$

which means that solids are being delivered to the sediment segment more rapidly than the sediment is being removed via sedimentation. This implies a nonsteady-state behavior that may be realistic at short time scales but cannot persist indefinitely. Therefore, one can conclude that, for the general case considered in this receiving water segment, $r_2 < r_1$, and the sediment solids should be less contaminated than overlying water solids at steady state. Note that this result applies only for the situation where chemical is being discharged to the water column.

SEDIMENT DECAY AND UNEQUAL PARTITIONING

Physical Parameter Effects

The behavior of r_2/r_1 when both mechanisms, mass-dependent partitioning ($\pi_2 < \pi_1$) and sediment decay ($K_2 > 0$), are present is of interest. Consider first the behavior of r_2/r_1 as a function of the physical parameters: K_L and $(w_{rs} + w_s)$. Contours of r_2/r_1 are shown in Figure 3a for π_1 and π_2 and in Figure 3b for $\pi_1 = 10\pi_2$. The behavior of r_2/r_1 as $w_{rs} + w_s$ increases is the same for both cases, i.e., r_2/r_1 increases toward unity as $w_{rs} + w_s$ increases, since increasing the particle mixing tends to equalize the particulate concentrations.

9

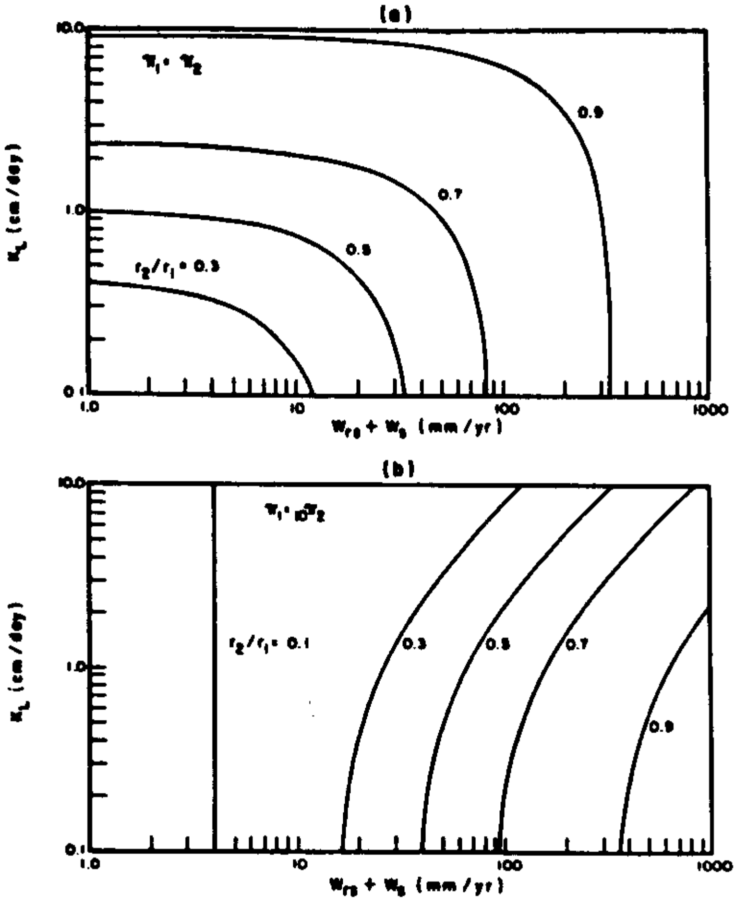


Figure 3. Contours of particulate concentration ration r_2/r_1 for $m_2 = 100{,}000$ mg/l, $H_2 = 1.0$ cm, $\pi_1 = 1000$ liter/kg, $K_2 = 0.01$/day.

However, the behavior of r_2/r_1 as K_L increases depends on π_2/π_1. For $\pi_2 = \pi_1$ (Figure 3a), the overlying and interstitial water-dissolved concentrations are in the same ratio as r_2/r_1, and increasing the diffusion tends to increase r_2/r_1 toward unity since the gradients of dissolved and particulate chemical are in the same direction. With $\pi_1/\pi_2 = 10$ (Figure 3b), the interstitial water to overlying water concentration ratio is:

$$\frac{c_{d2}}{c_{d1}} = \frac{\pi_1}{\pi_2} = 10\,\frac{r_2}{r_1} \tag{34}$$

Thus although r_2 is less than r_1, c_{d2} is greater than c_{d1} (for $r_2/r_1 > 0.1$), and increasing the diffusive mixing tends to remove chemical mass from the sediment, since relatively uncontaminated overlying water is now exchanging with more contaminated interstitial water. The effect is to transfer chemical mass from the sediment to the overlying water, thereby decreasing r_2 relative to r_1. This effect occurs so long as $r_2/r_1 > 0.1$, so that c_{d1} is smaller than c_{d2}. However at $r_2/r_1 = 0.1$, $c_{d1} = c_{d2}$, since it is assumed in this example that $\pi_1/\pi_2 = 10$ and varying K_L has no effect on r_2/r_1, since no dissolved chemical concentration gradient exists. This corresponds to the vertical contour in Figure 3b. For $r_2/r_1 < 0.1$, the contours would resemble Figure 3a, and increasing K_L would tend to increase r_2/r_1.

Chemical Parameter Effects

The behavior of r_2/r_1 as a function of the chemical parameters K_2 and π_2 is shown in Figure 4a for $\pi_1 = \pi_2$ and in Figure 4b for $\pi_1 = 10\pi_2$. Increasing K_2 decreases r_2/r_1 in both cases, as would be expected However, the effect of increasing π_2 depends on whether $\pi_1 = \pi_2$, in which case increasing π_2 reduces dissolved mixing and increases the residence time in the sediment so that decay can be more effective (Figure 4a). If $\pi_1 = 10\pi_2$ (Figure 4b), increasing π_2 inhibits the transfer of chemical mass from the sediment to the overlying water, thus increasing r_2/r_1.

Based on these results, it appears that the probable range for r_2/r_1 is 0.1-1.0 for $K_2 < 0.1$/day. Combining this information with the probable range of β of 0.01-100 suggests that the range of $\beta(r_2/r_1)$, which is the parameter group that directly determines the importance of the sediment removal mechanisms, $K_2 + K_s$ is in the range $\beta(r_2/r_1) = 0.001$-100.

OVERALL REACTION RATE

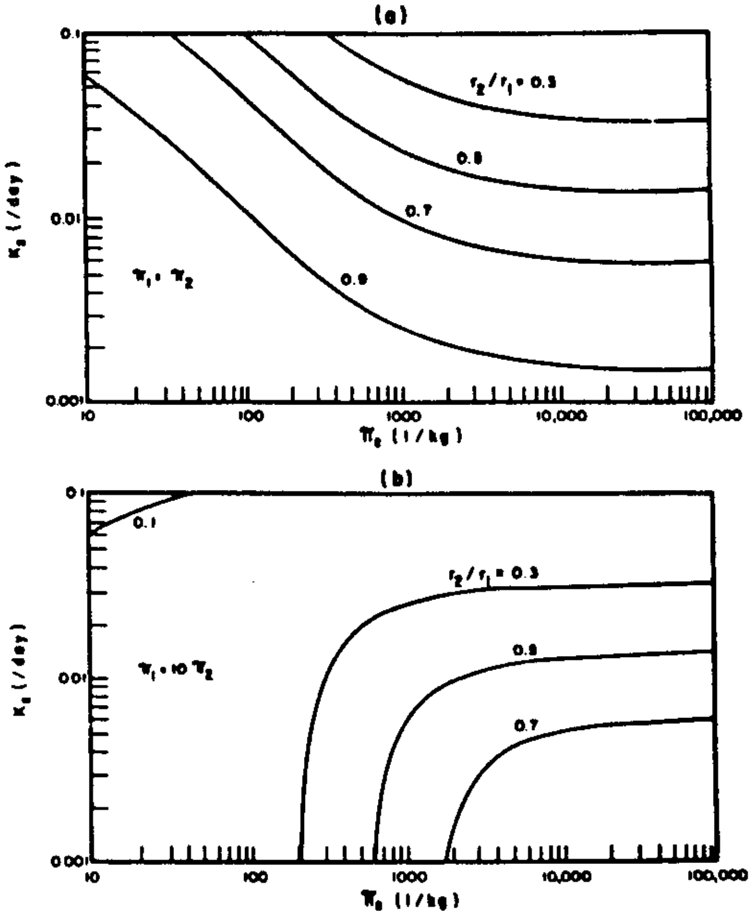


Figure 4. Contours of particulate concentration ratio r_2/r_1 for $w_n + w_s = 50$ mm/yr, $K_L = 1.0$ cm/day, $m_2 = 100{,}000$ mg/l, $H_2 = 1.0$ cm.

The probable range of K_T is determined by sediment decay rate (K_2) and the equivalent sedimentation removal rate (K_s). From reservoir sedimentation data, has been estimated to be in the range: $\beta K_s = 0.025$–0.5/day [4]. For r_2/r_1 in the range 0.1-1.0, the sedimentation sink is estimated to be in the range $\beta(r_2/r_1)K_s = 0.0025$–0.5/day.

Not much is known concerning the range of K_2 for the chemicals of concern; but if the probable range is $K_2 = 0$–0.1/day, then the range for $\beta(r_2/r_1)K_2 = 0$–10/day, the overall removal rate is:

$$K_T = K_1 + \beta \frac{r_2}{r_1} K_2 + \beta \frac{r_2}{r_1} K_s \qquad (35)$$

$$K_T = (0 - 0.1) + (0 - 10) + (0.0025 - 0.5)(/\text{day})$$

Hence even conservative chemicals (e.g., heavy metals, for which K_1 and K_2 are zero) can exhibit nonconservative behavior because of loss via sedimentation. Adding sediment decay can significantly increase the overall removal rate as can direct water column decay.

APPLICATION TO STREAMS AND RIVERS

The analysis of the fate of chemicals in streams and rivers is similar in many ways to the situation in lakes with what appears to be at first glance a significant difference. Whereas lakes can be represented, in many cases, by two completely mixed volumes, i.e., the water column and active sediment segments, the concern in a stream is with the longitudinal distribution of chemical downstream from the point of discharge. The key to the solution for this situation is shown in Figure 5. Consider the stream as being represented by a sequence of completely mixed volume segments. Let superscripts denote the segment being considered. Thus $c_{TI}^{(1)}$ is the water column chemical concentration in segment 1; $Q_I^{(1)}$ is the outflow rate; $t_{0I}^{(1)}$ is the detention time, and so on for all parameters.

The first stream segment receives a loading rate of chemical $W_{TI}^{(1)}$. Its outflow is $Q_I^{(1)}$, the flowrate of the stream. If longitudinal dispersion is neglected, then the first stream segment is exactly analogous to the situation analyzed previously. The equation for $c_{TI}^{(1)}$ is, as before:

$$c_{TI}^{(1)} = \frac{W_T^{(1)}/Q_I^{(1)}}{1 + K_T^{(1)} t_{0I}^{(1)}} \qquad (36)$$

where $c_{TI}^{(1)}$ = water column concentration
$t_{0I}^{(1)}$ = detention time of the first stream segment
$K_T^{(1)}$ = overall apparent removal rate evaluated using the parameters characteristic of the first segment

Consider the second completely mixed stream segment. The principal simplifying assumption to be employed in this analysis is that there is no horizontal bed motion. Although vertical sediment and interstitial water mixing is still being considered, horizontal bed motion is assumed not to be occurring. The reason for this assumption is that, for the fixed-bed case, the second stream segment receives only a water column input of chemical as a result of the stream flow from the upstream segment.

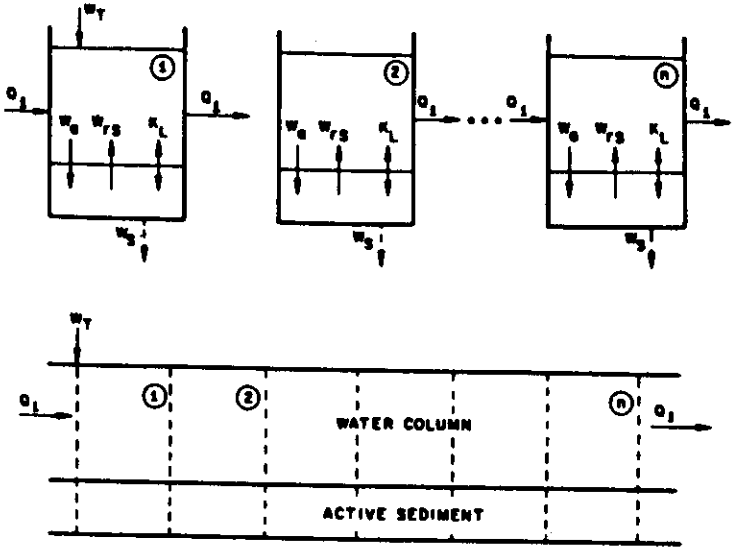


Figure 5. Representation of flowing streams as a sequence of receiving water segments.

$$W_{TI}^{(2)} = Q_I^{(1)} c_{TI}^{(1)} \qquad (37)$$

The key observation is that the second segment is also exactly analogous to the lake situation, and therefore its water column concentration is given by:

$$c_{TI}^{(2)} = \frac{W_{TI}^{(2)}/Q_I^{(2)}}{1 + K_T^{(2)} t_{0I}^{(2)}} \qquad (38)$$

where the superscript denotes the fact that all parameters are evaluated using the appropriate values for the second stream volume element. Note that it is not necessary that $Q_I^{(2)} = Q_I^{(1)}$ so that lateral inflow augmenting the streamflow is permitted in the analysis.

A similar argument applies to each stream volume element so that for the i^{th} element:

$$c_{TI}^{(i)} = \frac{W_{TI}^{(i)}/Q_I^{(i)}}{1 + K_T^{(i)} t_{0I}^{(i)}} \qquad (39)$$

and

$$W_{TI}^{(i)} = Q_I^{(i-1)} c_{TI}^{(i-1)} \tag{40}$$

For each volume element, $K_T^{(i)}$ is computed using the parameters characteristic of the i^th segment.

Equations 39 and 40 represent a complete solution of the fixed-bed stream case and are well suited to numerical computation. The stream volume elements are chosen to be small enough so that the longitudinal change in all parameters is small between adjacent segments and the longitudinal gradient of concentration is well represented. A simple criterion that ensures this to be the case is that $K_T^{(i)} t_{0I}^{(i)} < 0.1$. However, as with most general solutions, these equations provide little insight into the solution behavior.

Consider an idealized situation for which all physical, transport and reaction parameters are constant with respect to distance. This may well be an adequate representation of a section of a stream that has fairly uniform characteristics. In particular it is assumed that the water column and active sediment solids concentrations and depths are constant, together with reaction rates and vertical transport coefficients. For this case, the water column concentrations become, from Equation 36:

$$c_{TI}^{(1)} = \frac{W_{TI}/Q_I}{1 + K_T t_{0I}} \tag{41}$$

and, from Equations 37 and 38:

$$c_{TI}^{(2)} = \frac{Q_I c_{TI}^{(1)}/Q_I}{1 + K_T t_{0I}} = \frac{W_{TI}}{Q_I} \frac{1}{(1 + K_T t_{0I})^2} \tag{42}$$

so that the n^th volume element concentration becomes:

$$c_{TI}^{(n)} = \frac{W_{TI}}{Q_I} \frac{1}{(1 + K_T t_{0I})^n} \tag{43}$$

The arbitrary parameter in this formulation is the detention time (t_{0I}) since it depends on the volume (V_I) of each stream segment. Note that no other parameter involves V_I.

The method of removing V_I from this solution uses the following device. Let the volume size shrink to zero and at the same time let the number of volumes increase to infinity. The mathematical form of the argument is to define V_I as the product of the stream water column cross-sectional area A_I and a length Δx. That is, $V_I = \Delta x A_I$, and the detention time becomes:

$$t_{0I} = \frac{V_I}{Q_I} = \Delta x \frac{A_I}{Q_I} = \frac{\Delta x}{U_I} \tag{44}$$

where U_I = water column longitudinal velocity

Consider a location at a distance x from the location of the discharge. If Δx is the length of each stream volume segment, then the number of stream volume segments between the discharge location, which is taken to be $x = 0$, and location x is:

$$n = \frac{x}{\Delta x} \tag{45}$$

so that the water column concentration $c_{TI}^{(n)} = c_{TI}(x)$ becomes, from Equation 43:

$$c_{TI}(x) = \frac{W_{TI}}{Q_I} \left(1 + \frac{K_T \Delta x}{U_I}\right)^{-x/\Delta x} \tag{46}$$

Now letting $\Delta x \to 0$ and using the limit:

$$\lim_{y \to 0} \left(\frac{1}{1 + ay}\right)^{1/y} = e^{-a} \tag{47}$$

yields:

$$c_{TI}(x) = \frac{W_{TI}}{Q_I} \exp\left(\frac{-K_T x}{U_I}\right) \tag{48}$$

This remarkably simple result is exactly analogous to the solution for the longitudinal distribution of a nonconservative substance, which decays following a first-order reaction with rate coefficient K_T in the water column only. Hence, K_T plays exactly the same role in the stream model for partitioning chemicals as it does in the lake model. It is the apparent overall decay rate that accounts for both water column decay and sediment water interaction and decay. The expression for K_T is the same as before, as is r_2/r_1; and since all of the parameters are assumed to be constant in the reach of stream being considered, r_2/r_1 is seen to be independent of location. This is, at first glance, quite unexpected, since the longitudinal distribution of water column concentration is decreasing exponentially, and it should follow that the sediment concentration is decreasing as well. That is indeed the case since:

$$c_{T2}(x) = \beta \frac{r_2 H_1}{r_1 H_2} c_{T1}(x) \tag{49}$$

which follows directly from the definitions of r_2 and r_1. Thus c_{T2} is also decreasing exponentially, but r_2/r_1 is constant.

The reason that r_2/r_1 is independent of water column concentration and stream flow, just as it was independent of loading rate and detention time in the lake setting, is as follows: at any location x, particles being mixed vertically by resuspension and settling, and interstitial water mixing with overlying water react locally with whatever the overlying water concentration is at that location. At steady-state equilibrium, r_2/r_1 is independent of water column conditions, as is the ratio of interstitial water to overlying water $[c_{d2}/c_{d1} = (\pi_1/\pi_2)(r_2/r_1)]$ for the same reason that they are independent of water column conditions in the lake setting: all reactions are assumed to be first-order, and transport and chemical partitioning are linear with respect to concentration. Hence, considering ratios eliminates the absolute dependence on concentrations.

Therefore, analysis of the distribution of chemicals in flowing streams follows the same principles outlined in the analysis of lakes, and all the investigations of the behavior of the sediment capacity factor and r_2/r_1 as a function of parameter values are directly applicable. It is for this reason that the behavior of these fundamental parameters is crucial to the understanding of fate of chemicals in general. It can be shown that this reasoning applies to estuaries as well, as long as horizontal bed transport is not significant.

POSTSCRIPT

The above analysis is a good example of the insight that can be gained from a properly formulated analytical solution. The relative importance and interactions of the 13 parameters W_T/Q_1, t_{01}, m_1, H_1, m_2, H_2, K_1, K_2, π_1, π_2, K_L, w_n and w_s in determining the resulting receiving water and sediment concentrations can be pursued rationally. The importance of the dimensionless expressions for sediment capacity factor β and the central role played by the ratio of particulate concentrations r_2/r_1 becomes clear. The symmetry between lake and stream models is also apparent. An intuitive understanding of the situation can be gained, which, together with a feel for the relative magnitudes involved, can provide a degree of insight into a specific problem setting that is not otherwise attainable.

Contrast this situation to that which one faces when the problem is apparently so complex that only computer-based solutions are possible. Even when this is the case and a numerical computation is required, without the insight gained from the analysis of simplified situations, it is not possible to react intelligently to the numerical results. Apparently counterintuitive results are difficult to explain and even more difficult to check. Imagine one's response, for example, to computational results that indicated that increasing or decreasing sediment-water transport had no effect on the resulting water column and sediment concentrations. For the models analyzed in this paper, the reason for such behavior is clear: it occurs whenever $r_2 = r_1$. Whether this would be evident after an investigation of purely numerical results is uncertain, but our experience has been that insight is most rapidly and surely gained by an investigation of the structure of a properly posed and analyzed idealization.

ACKNOWLEDGMENTS

The results described in this chapter are part of a project report "Analysis of Fate of Chemicals in Receiving Waters" (CMA Project ENV-7-W) prepared by HydroQual for the Chemical Manufacturers Association. The authors gratefully acknowledge the assistance of the Chemical Manufacturers Association's Aquatic Research Task Group past and present members: R. E. Bailey, W. Bishop, J. L. Hamelink, R. A. Kimerle, E. C. Ladd, A. H. Lasday, G. Loewengart, R. J. Moolenaar, C. F. Muska, W. Pagano, C. P. Priesing, R. J. Samelson and W. F. Tully; and Chemical Manufacturers Association personnel: G. V. Cox and R. R. Romano for their interest, technical guidance and support throughout this project. Members of the HydroQual technical staff who have contributed to this project are James J. Fitzpatrick, Michael T. Kontaxis, Paul R. Paquin and Thomas W. Gallagher.

The project report and a computer program that implements the calculations discussed in this paper are available for a nominal fee from the Chemical Manufacturers Association.

REFERENCES

1. Smith, J. H., W. R. Mabey, N. Bohonos, B. R. Hold, S. S. Lei, T. W. Chow, D. C. Bomberger and T. Mill. "Environmental Pathways of Selected Chemicals in Freshwater Systems," U.S. EPA Report 600/7-77-113 (1977).

Environmental Toxicology and Chemistry, Vol. 3, pp. 335-353, 1984
Printed in the USA. Pergamon Press Ltd.

0730-7268/84 $3.00 + .00

TIME VARIABLE MODEL OF THE FATE OF DDE AND LINDANE IN A QUARRY

DOMINIC M. DI TORO[1,2] and PAUL R. PAQUIN[2]

[1]Environmental Engineering and Science Program
Manhattan College
Bronx, NY 10471
and
[2]HydroQual, Inc.
1 Lethbridge Plaza
Mahwah, NJ 07430

(*Received* 10 *May* 1983; *Accepted* 23 *November* 1983)

Abstract — A time variable model has been used to analyze a field scale experiment in which a flooded limestone quarry was dosed with equal quantities of Lindane and DDE. The water column and sediment chemical concentrations were monitored for one year after the initial dosing. The markedly different physical-chemical characteristics of the test chemicals provided an interesting contrast for model application.

A simplified time variable model of partitioning chemicals is cast in the form of analytical solutions for the total, dissolved and particulate concentrations of chemical in completely mixed, interactive, water column and sediment compartments. The model formulation incorporates chemical decay and transport mechanisms of particulate and diffusive exchange between water column and sediment. The Lindane and DDE model calibrations based on data from the first year after dosing are presented. A preliminary verification of the model, obtained by projecting DDE levels in the water and sediment five years after initial dosing, when the quarry was revisited, is also shown. The model results underscore the significance of chemical partitioning on chemical fate and highlight the importance and utility of a modeling framework which incorporates realistic mechanisms of water column and sediment interaction.

Keywords — Partitioning Fate Calibration Lindane DDE

INTRODUCTION

The evaluation of the fate of chemicals in the environment requires the use of a modeling framework which incorporates various idealizations of the transport and reaction mechanisms that are thought to be important. The validity of such models can only be established by careful calibrations and verifications using field data sets. A number of applications of this type have been reported [1] which illustrate to various degrees that realistic simulations of observed chemical behavior are possible. However, rigorous tests are not yet available. The major problems are the lack of reliable estimates of chemical mass discharge rates and independent measurements of transport and reaction rates. Controlled field scale experiments provide a useful source of these data. The purpose of this paper is to present an analysis of such an experiment.

An abandoned, flooded limestone quarry provided the setting for the field scale experiment which is the basis of the investigation described herein [2]. The time history of spike releases of DDE and Lindane was monitored in the biotic and abiotic sectors of the quarry water column and sediment for a period of approximately one year after the initial release. The experiment was performed under relatively controlled environmental conditions which were not subject to complicating factors such as a variable inflow, outflow, or loading history. The time variable nature of the experiment was a desirable feature since it enhances the importance of certain model parameters which are of lesser significance in steady state situations.

Presented at the Third Annual Meeting, Society of Environmental Toxicology and Chemistry, Arlington, VA, November 14-17, 1982.

CHRONOLOGICAL REVIEW AND DATA PRESENTATION

The quarry experiment was initiated during May of 1972. Pre-dosing levels of DDE and Lindane were measured and found to be negligible. A known mass of each chemical was uniformly distributed over the surface of the quarry on June 27, 1972 and on the following day, samples were collected for analysis of post release initial conditions in the water column, sediment and biota. Subsequent samples were collected on Days 5, 10, 21, 42 and at progressively longer time intervals over the course of the next year. The water column and sediment were usually sampled at various depths.

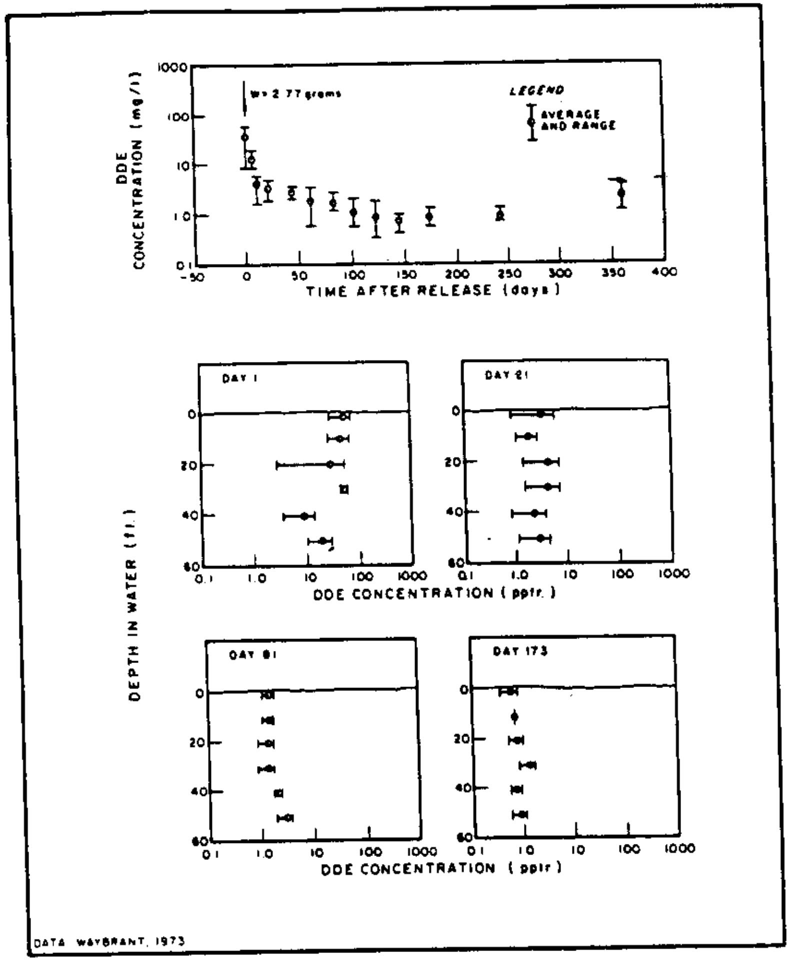
An intense rainfall occurred on the day after chemical addition, resulting in a significant influx of particles to the epilimnion of the thermally stratified quarry. Sedimentation trap data indicated that 2920 kg of solids entered the quarry and settled from the water between days 0 to 21. As will be shown, settling of these particles had a significant effect on the fate of both DDE and Lindane, chemicals with markedly different adsorptive characteristics.

As shown on Figure 1, the chronological plot of water column DDE concentration, the initial input of 2.77 g of DDE resulted in a depth averaged concentration on Day 1 of about 44 ng/L. This concentration was reduced to less than 10 ng/L by Day 10 and then gradually decreased to 1 ng/L by Day 100. A DDE concentration of about 1 ng/L persisted for the duration of the monitoring effort, although an increase to 3 ng/L was reported on Day 360, at the termination of the monitoring program.

The lower graphs in Figure 1 illustrate vertical profiles of DDE in the water column on selected days. Some vertical stratification is exhibited on Day 1, with average concentrations of 50 ng/L to a depth of 9 m and 10 to 20 ng/L at depths of 12 and 15 m. Although the fall overturn did not occur until Day 144, a relatively homogeneous vertical concentration profile was established by Day 21, and persisted for the duration of the study.

Sediment DDE data for the upper 1.5 cm of bottom sediment (μg DDE/kg wet sediment) are summarized in the upper panel of Figure 2. The sediment DDE concentration on Day 1 was quite low, but increased sharply to about 20 μg/kg by Day 5 and this concentration persisted for about 50 days. Although the results are variable, the average concentration increased to about 30 μg/kg for the next three sampling dates and then decreased to about 20 μg/kg on Day 241, the final day for which sediment data are available. As shown in the lower graphs, sediment samples from depths of 0 to 1.5, 1.5 to 3.5 and 3.5 to 5.5 cm showed that DDE penetration was for the most part limited to the upper 1.5 cm sediment layer.

Several distinctly different characteristics were observed in the temporal distributions of water column and sediment Lindane concentrations, (Figures 3 and 4). Significantly higher water column concentrations of Lindane were observed throughout the study, with the minimum concentration approaching 10 ng/L, an order of magnitude higher than the corresponding DDE concentration, at the end of the study. The wide ranges in the water column concentrations preceding the fall overturn (Day 144) reflect the vertical gradient of chemical between the epilimnion and hypolimnion of the stratified water body. The

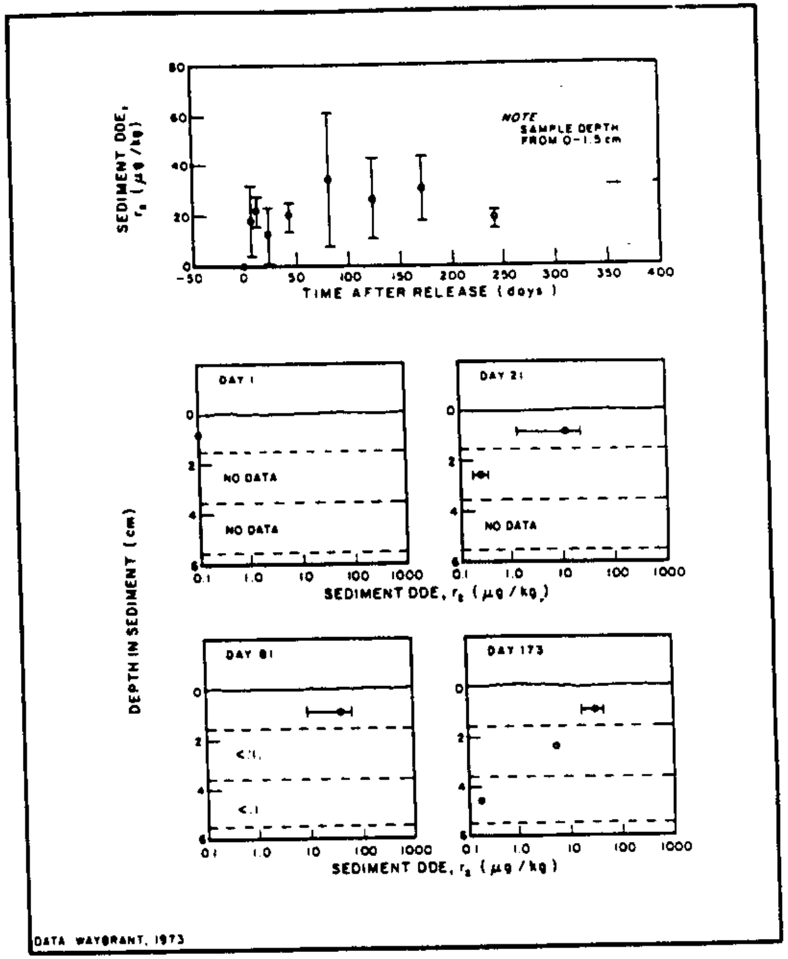


DATA WAYBRANT, 1973

Fig. 1. Temporal variation of DDE in water.

ranges are reduced after Day 144, when the water body was mixed by the fall overturn.

The vertical gradient of Lindane in the water column is more clearly illustrated in the four lower graphs of Figure 3. The concentration near the surface on Day 1 was more than 300 ng/L while at a depth of 15 m it was less than 10 ng/L. Vertical profiles on Days 21 and 81 also exhibited order of magnitude differences between the upper and lower layer average Lindane concentrations, in contrast to the DDE profiles which were nearly uniform at these same times. On Day 173, however, which followed the fall overturn, the physical mixing of the water body established a uniform vertical concentration profile in the water column.

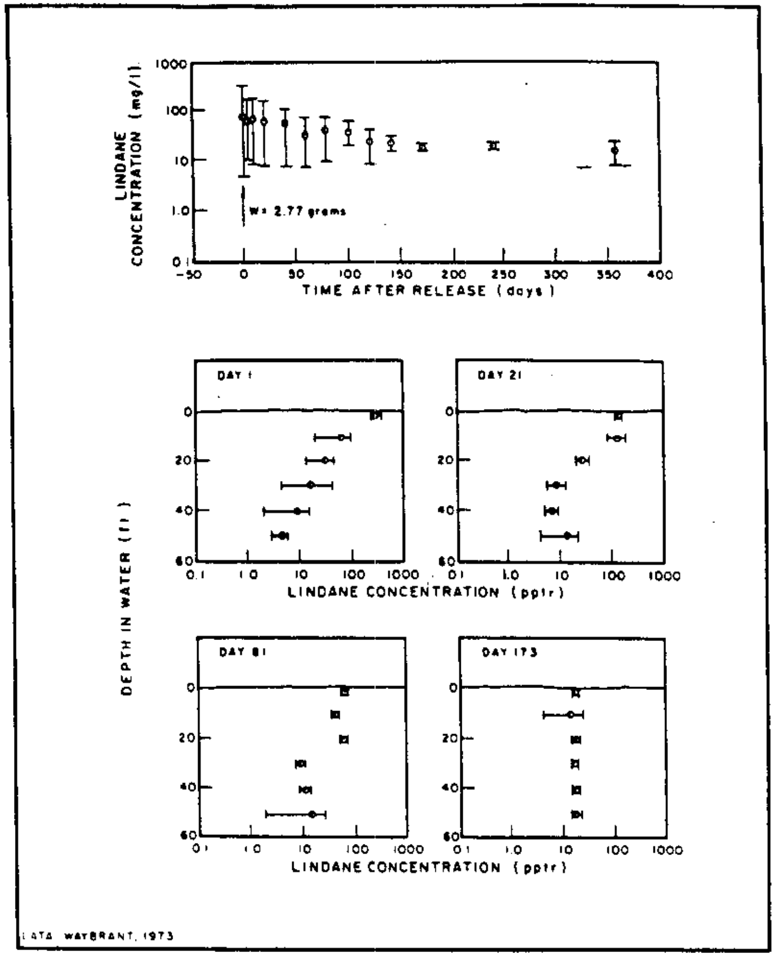


DATA WAYBRANT, 1973

Fig. 2. Temporal variation of DDE in sediment.

Sediment Lindane data are shown in Figure 4. With the exception of a sediment concentration of 7 µg/kg on Day 1, the sediment Lindane concentration averaged 1 to 2 µg/kg, an order of magnitude lower than sediment DDE levels. Lindane penetrated to the deeper sediment layer of 3.5 to 5.5 cm, and did not exhibit a pronounced vertical gradient. This is in contrast to the DDE results which were an order of magnitude higher in the surface layer, but at generally negligible levels at sediment depths greater than 1.5 cm.

Estimates of the mass of both DDE and Lindane associated with the water column, sediment, quarry walls, water surface film, fish, microcrustaceans and plankton were made [2]. Essentially, all of the chemical which was recovered was in the water col-



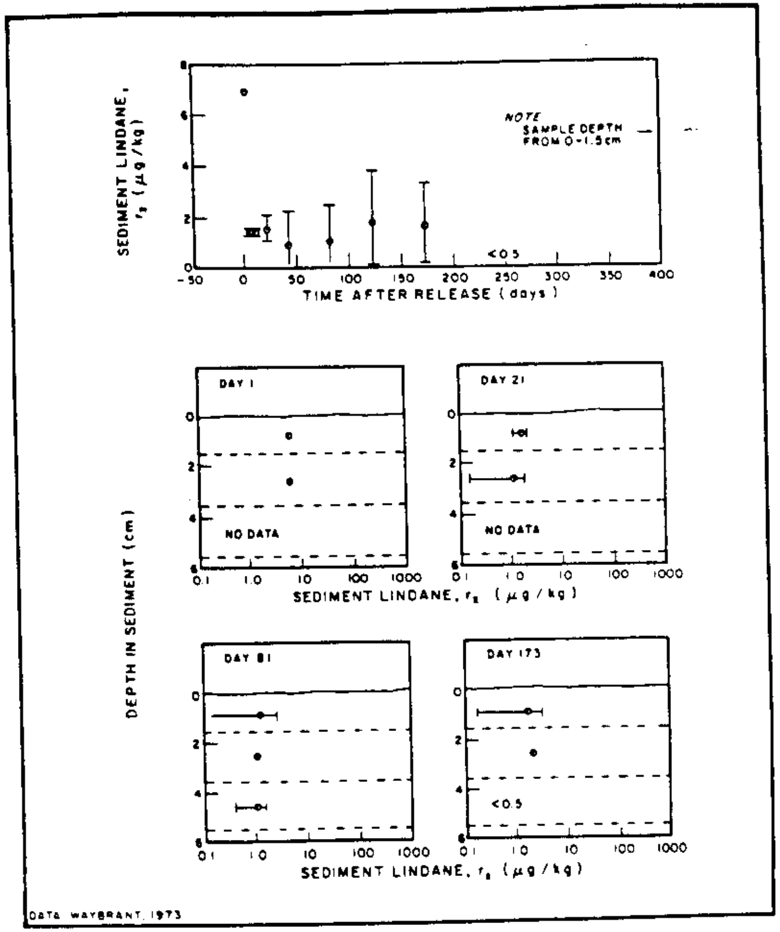
DATA WAYBRANT, 1973

Fig. 3. Temporal variation of Lindane in water.

umn and sediment and only a relatively small fraction was associated with the remaining compartments, which can, therefore, be neglected in the analysis of the fate of Lindane and DDE.

DESCRIPTION OF MODELING FRAMEWORK

The principal features of the modeling framework [3] are illustrated in Figure 5. An instantaneous release of chemical, M_T is discharged to a completely mixed receiving water of volume V_1 and depth H_1, where it undergoes dilution by the freshwater inflow, Q_1. The chemical is partitioned between the dissolved and particulate phases in the water column and sediment which have suspended solids concentrations of m_1



DATA WAYBRANT, 1973

Fig. 4. Temporal variation of Lindane in sediment.

and m_2 respectively. Chemical is transferred between the water column and sediment layer by settling and resuspension of contaminated particles and via diffusive exchange between the dissolved phases in the water and sediment. The chemical may also undergo first order decay in the water column and sediment or it may be removed from the system by sedimentation.

The solution for an instantaneous release of chemical of mass M_T is required. The initial water column concentration is simply $c_{T1}(o) = M_T/V_1$. The analytical solution for the time variable water column and sediment concentrations can be readily obtained [4]. The notation and general solutions (Eqns. 1–8) are listed in Tables 1 and 2. Equations 2A and 2B may be evaluated in time to obtain the total chemical concentrations in the water and sediment, $c_{T1}(t)$ and $c_{T2}(t)$, which result from initial conditions in the water column and sediment.

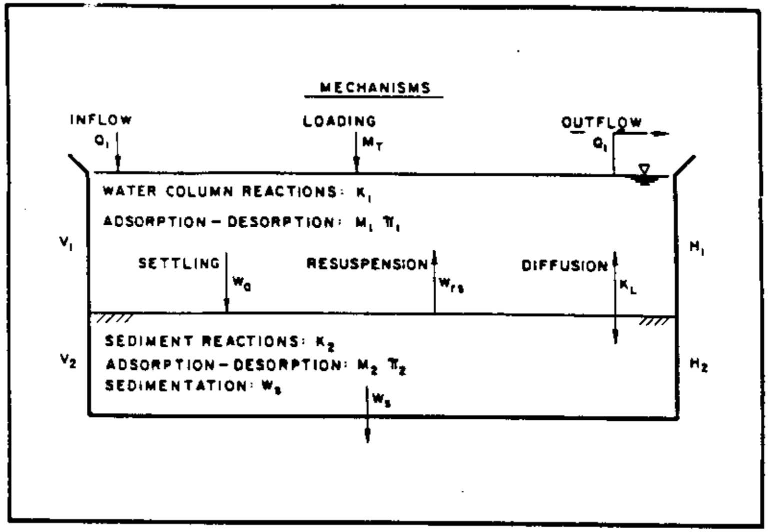


Fig. 5. Schematic of model framework.

Table 1. Definitions

Parameters	Water Column	Sediment
Chemical/Biological		
Loading (g)	M_T,	—
Sum of hydrolysis, oxidation, biodegradation, photolysis, volatilization rates (/day)	K_1	K_2
Partition coefficients (L/kg)	π_1	π_2
Physical		
Solids Concentration (mg/L)	m_1	m_2
Depth (m)	H_1	H_2
Volume (m^3)	V_1	V_2
Flow Rate (m^3/d)	Q_1	—
Detention Time (d)	$t_{01} = V_1/Q_1$	—
Settling Velocity (m/d)	w_a	—
Resuspension Velocity (mm/yr)	—	w_n
Diffusion Exchange Coefficient (cm/d)	—	K_L
Sedimentation Velocity (mm/yr) (Sedimentation Rate Coefficient, /d)	—	w_s $(k_s = w_s/H_2)$
Concentrations		
Total = Dissolved + Particulate (µg/L)	$c_{T1} = c_{d1} + c_{p1}$	$c_{T2} = c_{d2} + c_{p2}$
Particulate chemical ratio (µg chemical/g solids)	$r_1 = c_{p1}/m_1$	$r_2 = c_{p2}/m_2$
Chemical Phase Fractions		
Particulate: $f_p = \dfrac{\pi m/\phi}{1 + \pi m/\phi}$	f_{p1}	f_{p2}
Dissolved: $f_d = \dfrac{1}{1 + \pi m/\phi}$	f_{d1}	f_{d2}

Table 2. Solutions to mass balance equations

The differential equations which control the water column and sediment response are:

Water Column

$$\frac{dc_{T1}}{dt} = -K_1 c_{T1} - \frac{c_{T1}}{t_{01}} - \frac{K_L}{H_1}(f_{d1} c_{T1} - f_{d2} c_{T2}) - \frac{w_a}{H_1} f_{p1} c_{T1} + \frac{w_n f_{p2} c_{T2}}{H_1} + \frac{W_T}{V_1} \tag{1A}$$

$$\frac{dc_{T2}}{dt} = -K_2 c_{T2} + \frac{K_L}{H_2}(f_{d1} c_{T1} - f_{d2} c_{T2}) + \frac{w_a}{H_2} f_{p1} c_{T1} - \frac{w_n}{H_2} f_{p2} c_{T2} - \frac{w_s}{H_2} f_{p2} c_{T2} \tag{1B}$$

The analytical solutions are given by

Water Column

$$c_{T1}(t) = c_{T1}(0)\left[\frac{g_1 - s_2}{g_1 - g_2} e^{-g_1 t} + \frac{g_2 - s_2}{g_2 - g_1} e^{-g_2 t}\right] + c_{T2}(0)\,\frac{H_2}{H_1}\left(\frac{s_2 - K_2 - K_s}{g_1 - g_2}\right)(e^{-g_2 t} - e^{-g_1 t}) \tag{2A}$$

Sediment

$$c_{T2}(t) = c_{T2}(0)\left[\frac{g_1 - s_1'}{g_1 - g_2} e^{-g_1 t} + \frac{g_2 - s_1'}{g_2 - g_1} e^{-g_2 t}\right] + c_{T1}(0)\,\beta\,\frac{r_2}{r_1}\,\frac{H_1}{H_2}\,\frac{s_2}{g_1 - g_2}\left[e^{-g_2 t} - e^{-g_1 t}\right] \tag{2B}$$

where g_1 and g_2 are evaluated using the positive and negative terms respectively of the following expression:

$$g_1, g_2 = \left[\frac{s_T + 1/t_{01}}{2}\right] \cdot \left[1 \pm \left(1 - \frac{4(s_2(K_1 + 1/t_{01}) + (K_2 + K_s)(s_1 - K_1))}{(s_T + 1/t_{01})^2}\right)^{1/2}\right] \tag{3}$$

Here,

$$s_1 = K_1 + (w_a f_{p1} + K_L f_{d1})/H_1$$

$$s_2 = K_2 + [(w_n + w_s) f_{p2} + K_L f_{d2}]/H_2 \tag{4}$$

$$s_T = s_1 + s_2 \tag{5}$$

and $s_1' = s_1 + 1/t_{01}$. The sediment capacity factor is given by (6)

$$\beta = \frac{m_2 H_2 f_{p1}}{m_1 H_1 f_{p2}} \tag{7}$$

As shown elsewhere (4) the ratio of the steady state particulate chemical concentrations in the sediment and water, r_2/r_1, may be expressed as:

$$\frac{r_2}{r_1} = \frac{w_a (m_1/m_2) f_{p2} + K_L (\pi_2/\pi_1 \phi_2) f_{d2}}{(w_n + w_s) f_{p2} + K_L f_{d2} + K_2 H_2} \tag{8}$$

Approximate forms for the roots of the quadratic Equation 3 have been found [4] and these greatly simplify the solution:

$$g_1 = s_1' + s_2 \tag{9}$$

$$g_2 = \frac{s_2}{s_1' + s_2} K_T \tag{10}$$

where $K_T = K_1 + \beta(r_2/r_1)(K_2 + K_s)$. The detention time of the quarry is very long and $s_{1'} = s_1$. Using these approximate roots, the solutions become:

$$c_{T1}(t) = c_{T1}(0)\left[\frac{s_1}{s_1 + s_2} e^{-g_1 t} + \frac{s_2}{s_1 + s_2} e^{-g_2 t}\right] + c_{T2}(0)\,\frac{H_2}{H_1}\,\frac{s_2}{s_1 + s_2}\,[e^{-g_2 t} - e^{-g_1 t}] \tag{11}$$

$$c_{T2}(t) = c_{T2}(0)\left[\frac{s_2}{s_1 + s_2} e^{-g_1 t} + \frac{s_1}{s_1 + s_2} e^{-g_2 t}\right] + c_{T1}(0)\,\beta\,\frac{r_2}{r_1}\,\frac{H_1}{H_2}\,\frac{s_2}{s_1 + s_2}\,[e^{-g_2 t} - e^{-g_1 t}] \tag{12}$$

Two important features of general interest can be seen in these simplifications. The concentrations are determined by two terms: s_1, which is the sum of the water column decay and sediment transfer fluxes; and s_2 which is the analogous sum of sediment decay and water transfer fluxes. The "fast" decay rate, g_1, is simply the sum of s_1 and s_2 and represents the rate at which water column and sediment concentrations initially equilibrate. The "slow" decay rate, g_2, is a fraction $(s_2/(s_1+ s_2))$ of the total equivalent removal rate, K_T, which is the parameter that controls the steady state water column concentration, $c_{T1}(\infty)$, if the mass input rate were constant, W_T. That is: $c_{T1}(\infty) = (W_T/Q_1)/(1 + K_T t_{01})$. Thus, a straightforward calculation of g_2 gives immediately the half life $(= 0.693/g_2)$ to be expected as a function of the relevant physical and chemical properties.

MODEL PARAMETERS

Based on a review of long-term climatological records, it was found that the difference between average annual precipitation (~ 100 cm/yr) and evaporation (~ 85 cm/yr) in the vicinity of the quarry, 15 cm, is insignificant in comparison to the overall depth of water in the quarry ($H_1 = 13.9$ m). It is, therefore, reasonable to assume constant geometry and no net inflow. The quarry itself was represented as a completely mixed water column and sediment layer. The depth of the active sediment layer is estimated from observed chemical penetration into the sediment. DDE was observed to penetrate, at most, the upper 1.5 cm of sediment while Lindane penetrated to a depth of at least 5.5 cm (Figs. 2 and 4). Thus, chemical specific sediment layer depths of $H_2 = 1.5$ cm and 5.5 cm were used to characterize DDE and Lindane respectively. The use of different sediment layer depths is necessitated by the simplified representation of diffusive exchange and the assumption of a completely mixed sediment layer incorporated in the modeling framework.

The mass loadings of interest are the chemical and solids flux rates to the quarry. The chemical inputs of DDE and Lindane were accurately measured. Sedimentation trap data was used to estimate the mass of sediment which entered the quarry between Days 0 and 21. The analysis of particulate transport in the quarry is complicated by the lack of field measurements of the suspended solids concentrations in the water column and sediment, m_1 and m_2, respectively. Sediment trap and secchi depth data were used as the basis for characterizing the temporal variation of m_1. Empirical correlations with secchi depth measurements indicated that pre-rainstorm suspended solids levels were about 5 mg/L. Assuming the added material settled out of the water between days 0 to 10, from the temporal variation of the DDE water column data, the settling rate w_a and average suspended solids concentration, m_1, are fixed by the measured solids flux.

The Secchi disc readings after the initial period were generally 6 to 7 m, and aside from some initial variability which was attributed to algal effects [2] the readings were essentially constant in time. There were no other sources of solids to the quarry and since resuspension was probably negligible, w_a was likely to have been much lower than the 3.2 m/d estimated for the first 10 d. In view of these considerations, $w_a = 0.1$ m/d was assigned for $t > 10$ d. This settling velocity essentially eliminates particulate transport as a mechanism of chemical transfer after Day 10. The use of a variable settling velocity is considered reasonable since it is likely that relatively coarse particles entered the quarry as a result of the intense storm on Day 1, and these would settle rapidly. The remaining particles are either settling much more slowly or not at all.

The sediment solids concentration is also required to perform the analysis. From reported water volumes in sediment samples the sediment porosity is estimated to be $\phi = 0.45$, and from the reported bulk density of the sediment $\rho_b = 1.2$ g/cc, $m_2 = \rho_b - \phi\rho_s = 750$ g/L. The sedimentation velocity, w_s, was set to zero because the net chemical

transfer to the deep, inactive sediment was not considered as a loss of chemical from the system.

CHEMICAL TRANSFERS AND KINETICS

Limited data were available to characterize DDE and Lindane partition coefficients. Estimates of the DDE partition coefficient were based on the partition coefficient for DDT due to the similarity of the octanol/water partition coefficients [5]. At solids concentrations on the order of 10 mg/L, as in the quarry, available DDT data [6], shown in the upper panel of Figure 6, indicate a range of 50,000 L/kg on illite clay to 275,000 L/kg on montmorillonite clay. Figure 6 also illustrates the inverse relationship

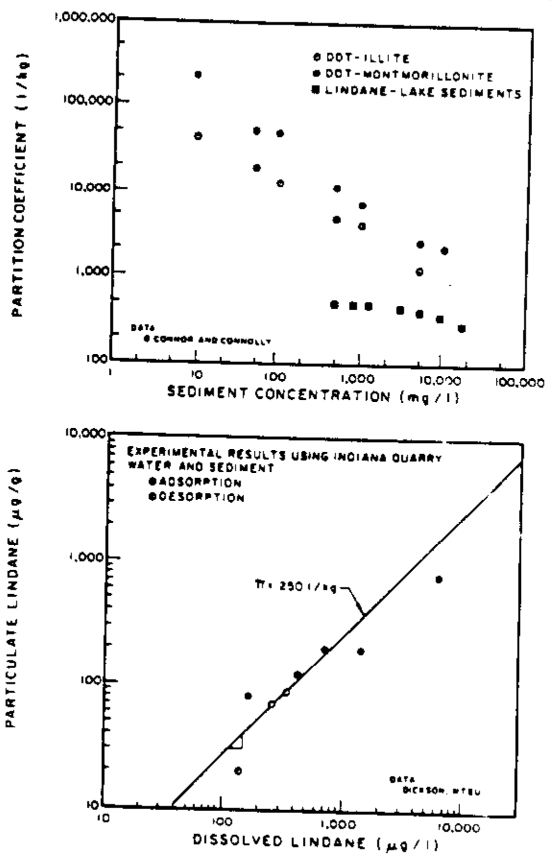


Fig. 6. Lindane and DDT adsorption-desorption data.

between partition coefficient, π, and suspended solids concentration. It is expected that this trend would also apply to the quarry, although the slope may be different as a result of differences in the characteristics of the solids.

The lower panel of Figure 6 shows Lindane isotherm data obtained using water and solids from the quarry [7], and an average partition coefficient of π = 250 L/kg provides a good fit of these data. Suspended solids concentration dependent partitioning has also been observed with Lindane (upper panel). From the limited available data, however, it is difficult to estimate π_2 for either chemical at the estimated sediment solids concentration in the quarry of m_2 = 750 g/L. Thus, π_2 is not well defined and should be viewed as a calibration parameter.

Diffusive exchange

The diffusive exchange coefficient, K_L, was estimated to be 50 cm/d from microcosm experiments performed with Lindane [8]. Since DDE and Lindane have comparable molecular weights (352 and 291, respectively), a value of K_L = 50 cm/d has been used for both compounds. This parameter should also be viewed as a calibrated value since no direct measurement is available for the quarry.

Chemical decay

DDE and Lindane decay rates used in the modeling analysis are summarized in Table 3. The most significant decay rate for Lindane, hydrolysis, was estimated from laboratory experiments [7] to range from .0018 to .0257/d. A rate at the lower end of this range (.0025/d) was needed to fit the field data. Information on photolysis and volatilization [7] suggested that losses of Lindane by these mechanisms occurred at an order of magnitude lower rate than hydrolysis.

The only significant loss rates for DDE were found to be photolysis and volatilization. An average annual photolysis rate of .013/d was estimated following the approach of Zepp [9]. A somewhat higher volatilization rate of .020/d was estimated from laboratory results [10]. The total water column decay rate for DDE of 0.033/d is thus an order of magnitude higher than the Lindane decay rate, suggesting that Lindane would be the more persistent chemical.

MODEL CALIBRATION — LINDANE

Physical and chemical parameters for Lindane and DDE were estimated in previous sections. It remains to compare the computed results and observed data and establish final values for calibration parameters. The difference in solids behavior during the first 10 d following the storm (the initial period) and subsequently (the second period) requires that the analysis be done in two steps. The procedure is to calculate the chemical concentrations in the water column and sediment for the first 10 d using the appropriate initial period parameter values. Then, using the calculated water column and sediment concentrations at Day 10 as initial conditions, continue the calculation using the parameters that are appropriate for the second period. These parameters are listed in Table 4.

The calculated and observed Lindane distributions are shown in Figure 7 using linear and logarithmic concentration scales for the water column. The predicted initial rapid decrease of Lindane is somewhat overestimated. This is due to the stratified conditions in the quarry during the initial 100 days (see Fig. 3) which prevented the Lindane from being vertically well-mixed, as is assumed in the model. This discrepancy is also apparent in the sediment calculation. After vertical mixing, however, the comparison is satisfactory.

A better understanding of the behavior of Lindane in the quarry can be obtained by considering the form of the simplified analytical solutions, Equations 11 and 12, and the relative magnitudes of the parameters affecting chemical fate. As can be seen in Table 4, the differing water column solids concentrations (m_1 = 24 mg/L → 5 mg/L) and settling velocities (w_s = 3.2 m/d → 0.1 m/d) have only a small effect on the relevant rates that control the chemical fate of Lindane. This is due to the relatively low partition coefficient of Lindane, which at these solids concentrations, results in most of the Lindane being the dissolved fraction in the water column (f_{d1} = 0.9940 → 0.9988). Thus particle transport is small relative to diffusive exchange as the mechanism which transfers Lindane from the water column to the sediment.

The total water column transfer-decay rate, s_1, is dominated by the diffusive exchange rate: $K_L f_{d1}/H_1$ as is the total sediment transfer-decay rate, $s_2 = K_L f_{d2}/H_2$. As can be seen from the form of the solution for the water column Lindane concentration, c_{T1}, these rates control the relative amount of Lindane which is initially transferred to the sediment via diffusive exchange ($s_1/(s_1 + s_2)$ = 27%) and that which remains in the

Table 3. Summary of DDE and Lindane decay coefficients (L/d)

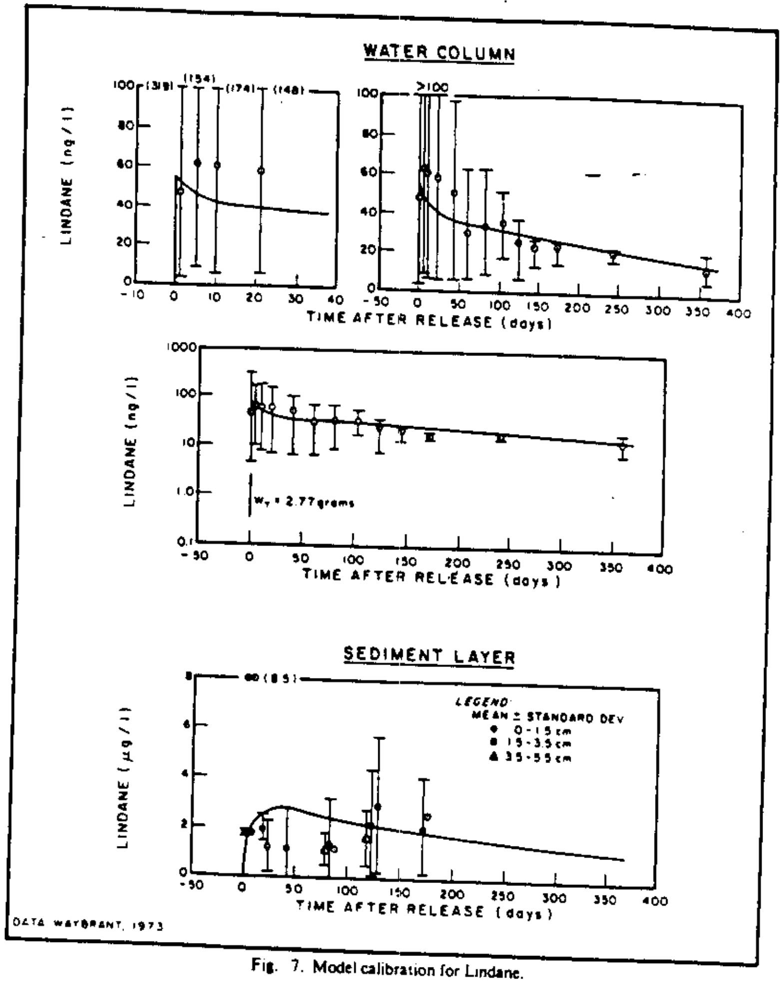
	Lindane		DDE	
	Water	Sediment	Water	Sediment
Hydrolysis	.0018-.0257[a]	.0018-.0257[a]	0.0	0.0
Oxidation	0.0	0.0	0.0	0.0
Biolysis	0.0	0.0	0.0	0.0
Photolysis	.00026	—	0.013	—
Volatilization	.00018	—	0.020	—

[a] Used .0025/d for calibration and projections

Table 4. Summary of chemical physical parameters used in calibration analysis[a]

		Lindane		DDE	
	Units	Water Column	Sediment Layer	Water Column	Sediment Layer
Chemical/Physical Parameters:					
Depth	m	3.9	.055	13.9	.015
Suspended Solids	mg/L	24.0/5.0	7.5×10^5	24.0/5.0	7.5×10^5
Particle Velocities					
Settling	m/d	3.2/0.1	—	3.2/0.1	—
Resuspension	mm/yr	—	0.0	—	0.0
Sedimentation	mm/yr	—	0.0	—	0.0
Diffusive Exchange	cm/d	50.		50.	
Partition Coefficient	L/kg	250.	50.0	50,000.	10,000.
Dissolved Fraction		.9940/.9988	.0118	.4545/.8000	.00006
Particulate Fraction		.0060/.0012	.9882	.5455/.2000	.99994
Total Removal Rate	L/d	.0029	.0025	.0330	0.0
Model Related Parameters:					
Sediment Capacity Factor, β		.7460/.7490		18.4/32.4	
Particulate Concentration Ratio, r_2/r_1		.4524/.4358		3.87/.47	
Total Apparent Removal Rate, K_T	L/d	.0037/.0037		.0329/.0329	
Total Transfer-Decay Rates					
Water Column, s_1	L/d	.0401/.0389		.1749/.0632	
Sediment Layer, s_2	L/d	.1099/.1099		.0020/.0020	
Fast Decay Rate, g_1	L/d	.1472/.1460		.1766/.0643	
Slow Decay Rate, g_2	L/d	.0029/.0029		.00037/.00106	
Half Life, .693/g_2	d	239./239.		1870./693.	

[a] Parameter values for t < 10 days/t ≥ 10 days, when two values are shown.



DATA WAYBRANT, 1973

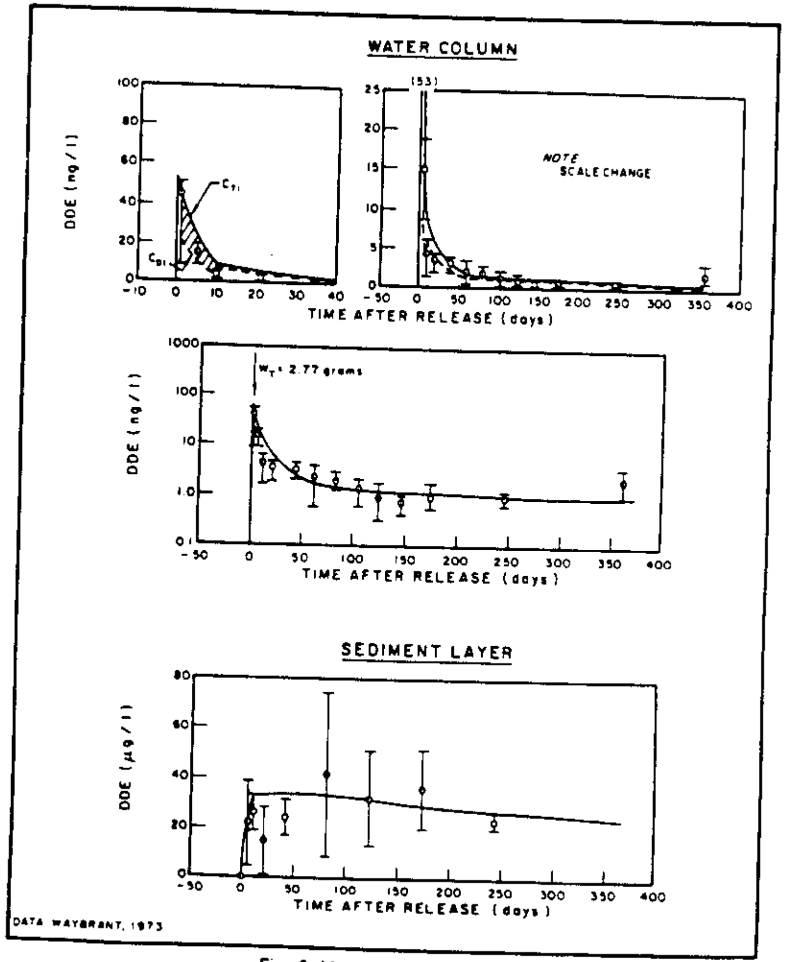
Fig. 7. Model calibration for Lindane.

water column ($s_2/(s_1 + {}_2) = 73\%$). These determine the rate at which the initial transfer takes place: $g_1 = s_1 + s_2 = 0.15/d$, and together with the total apparent removal rate, K_T, the slow overall loss rate: $g_2 = (s_2/s_1 + s_2)K_T = 0.0029/d$. The contribution of sediment decay, K_2, is small relative to water column decay even though they are both nearly equal ($K_1 = 0.0029/d$; $K_2 = 0.0025/d$). The reason is that $\beta r_2/r_1$ is small due to the relatively low partition coefficient for Lindane.

MODEL CALIBRATION — DDE

Differences in particulate transport between the initial ten days of rapid solids deposition and the subsequent period are important in determining the fate of DDE in

the quarry. The physical and chemical parameters for both periods are shown in Table 4, and a comparison of calculated and observed DDE distributions is presented in Figure 8. The calculated water column DDE concentrations in the two upper graphs of Figure 8 are in very good agreement with the data. During the first 10 days of the experiment the calculated and observed water column concentration decreased from about 53 ng/L to less than 10 ng/L, while the total sediment concentration of DDE increased sharply to more than 25 μg/L. The rapid decrease in the water column DDE and the corresponding increase in the sediment DDE is due to adsorption of DDE onto the water column solids which settle to the sediment. After Day 10,



DATA WAYBRANT, 1973

Fig. 8. Model calibration for DDE.

there is a much more gradual decrease in the water column DDE concentration, since the net flux of solids to the sediment is essentially zero.

The calculated sediment DDE concentration reaches a maximum of 34.5 μg/L by approximately Day 40, at which time a local equilibrium condition between the water column and sediment concentrations is approached. After Day 100, the calculated water column concentration of 1.3 ng/L decreases slowly, while the sediment concentration of slightly more than 30 μg/L decreases at a rate which is in proportion to the water column concentration. All removal of DDE occurs in the water column as a result of photolysis and volatilization. As the water column concentration decreases, DDE diffuses from the sediment interstitial water into the overlying water (the resuspension rate is zero), and the sediment concentration decreases: As long as there is water column decay, equilibrium conditions between dissolved concentrations in the water column and sediment layer interstitial water cannot be established and the decrease of water and sediment concentrations will continue until the DDE is depleted from the system.

It is of interest to further consider the computed total and dissolved DDE concentrations, both shown in the linear scale water column comparisons of Figure 8. The reported total DDE concentrations were actually measured after a glass wool filtration, which probably removed a significant portion of the adsorbed particulate DDE. Mass budget calculations [2] indicated an apparent loss of total DDE mass during this time period. The model computations suggest that the missing DDE was associated with the water column particles removed by the filtration.

Additional insight into the fate of DDE can be obtained by considering the analytical solutions and the magnitudes of the parameters affecting chemical fate. For the initial period, the total water column transfer-decay rate, s_1, is dominated by the solids settling velocity term. In contrast to the Lindane situation, the water column partition coefficient of DDE is large enough ($\pi_1 = 50{,}000$ L/kg) to make the particulate fraction significant ($f_{p1} = 0.545$) and removal by settling dominates over water column decay and diffusive exchange. By contrast, the total sediment transfer-decay rate, s_2, is controlled by the diffusive exchange rate, $K_L f_{d2}/H_2 = 0.002$/d which is substantially less than that for Lindane (0.107/d) due to the higher sediment partition coefficient of DDE. As a consequence, the initial rapid depletion of water column DDE and the corresponding sediment increase is entirely controlled by the fast decay rate:

$$g_1 = s_1 + s_2 \simeq w_s f_{p1}/H_1 \tag{14}$$

This fact is reflected in the choice of t = 10 days as the dividing point between the two periods. At the end of 10 d the sediment has increased in concentration to $c_{T2} = 32.6$ μg/L which is a tenfold greater concentration than that achieved by Lindane in the same time period. The difference is due to the markedly different mechanisms which transferred each chemical to the sediment: whereas diffusive exchange dominated Lindane transport, particle settling dominated DDE transport.

During the second period, the total water column transfer-decay rate, s_1, is dominated by diffusive exchange and water column decay as a result of reduced particle settling. The total sediment transfer-decay rate, s_2, is the same as during the initial period. As a result, the ratio controlling the slow decay rate, $s_2/s_1 + s_2$, increases markedly, as does the slow decay rate, g_2. The half life of DDE decreases almost threefold as a result of the decrease in settling velocity, since decay occurs only in the water column and settling provides a mechanism whereby DDE is transferred to the sediment.

The behavior of the water column concentration after the initial period can be viewed as the sum of the DDE responses due to the DDE in the water column and

that in the sediment at t = 10 d (t′ = 0). The formula that results is:

$$\begin{aligned} c_{T_1}(t) &= 8.93\,[0.968\,e^{-g_1 t'} + 0.032\,e^{-g_2 t'}] \\ &\quad + 1.12\,[e^{-g_2 t'} - e^{-g_1 t'}] \end{aligned} \tag{15}$$

where the first line is the water column concentration due to the initial condition in the water column, and the second line is the contribution due to the sediment initial condition. Note that a significant contribution to the early response (t′ ~ $3/g_1$ = 47 d, t = 57 d) is due to the initial condition in the water column. Thereafter, however, its importance diminishes and its contribution to the response is negligible. By contrast, the DDE initially in the sediment then controls the response and the water column concentration is determined by the g_2 decay terms. Both water column and sediment concentration are decaying with a half-life of about 700 d.

The importance of the various parameters can be understood as follows. The long term fate of DDE is controlled by the initial quantity deposited in the sediment during the first 10 d, which in turn is controlled by the rapid decay rate, $g_1 = w_s f_{p1}/H_1$. Hence, the settling velocity, water column partition coefficient and solids concentration is each important. The long term decay is determined by the slow rate:

$$g_2 = \frac{s_2}{s_1 + s_2} K_T \tag{16}$$

The ratio of the transfer-decay rates during the second period is dominated by the terms:

$$\frac{s_2}{s_1 + s_2} = \frac{K_L f_{d2}/H_2}{K_1 + K_L f_{d1}/H_1} = \frac{0.002}{0.033 + 0.0288} \tag{17}$$

The rate of diffusive exchange is of primary importance since it is this mechanism that is transferring DDE from the sediment to the water column, where it is subject to decay. Hence the diffusive exchange rate and the sediment parameters m_2 and π_2 (which affect f_{d2}) are both important. Finally, the water column decay rates for photolysis and volatilization are, of course, critical since they sum to form K_T which is the second factor in the slow rate expression, Equation [16].

Figure 9 compares the calculated masses of Lindane and DDE in the water column and sediment during the calibration period. On Day 100, 2.07 grams (75%) of the initial 2.77 grams of Lindane can be accounted for in the water column and sediment layer of the quarry. Of this amount, more than 75% is present in the water column. Similarly, 1.93 grams (70%) of the initial input of DDE also remains on Day 100. This is somewhat surprising, in view of the order of magnitude higher water column decay rate of DDE relative to Lindane. The persistence of DDE is directly related to the relatively high percentage of that chemical stored in the sediment and hence not available for photolysis or volatilization. The model calculations show that more than 96% of the remaining 1.93 grams of DDE in the system at Day 100 is in the sediment layer.

MODEL VERIFICATION AND PROJECTIONS

Approximately five years after the initial dosing of the quarry, on June 21, 1977, several sediment samples were collected and analyzed for DDE (R. G. Zepp, personal communication). Although this follow-up sampling and analysis was of limited scope, it provides a basis for a preliminary verification of the model.

Two methods were used for sampling; in each case the depth of sample was only known to within a rough approximation. The reported DDE concentrations on a solids mass basis were converted to volumetric concentrations and adjusted to concentration ranges which reflect the uncertainty in sampling depth and which correspond to an assumed depth of DDE penetration of 1.5 cm. These DDE concentration ranges, 3.4 to 11.2 μg/L for Sample A and 2.9 to 4.2 μg/L for Sample B, represent almost an order of magnitude decrease in the sediment DDE concentration since the time of the quarry experiment. The DDE level in water

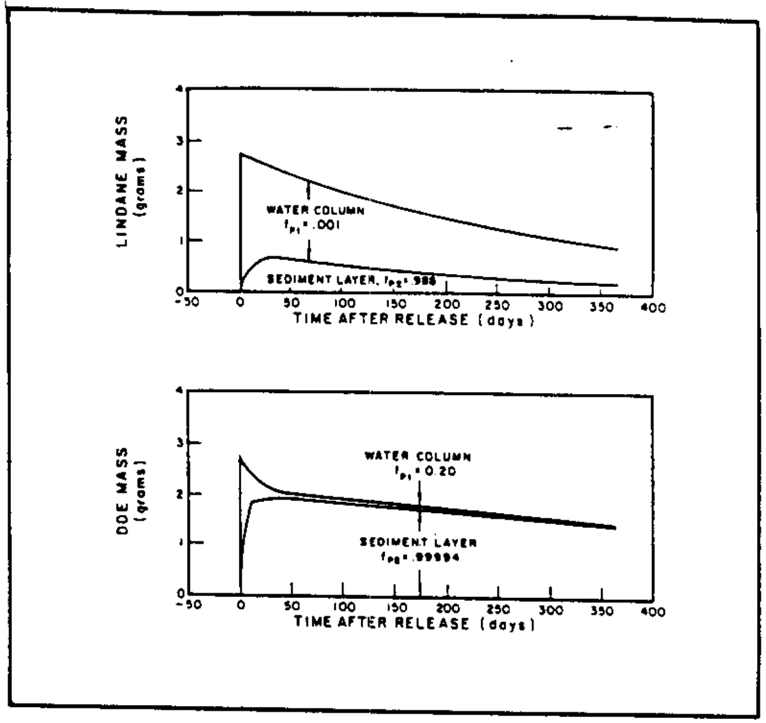


Fig. 9. Comparison of masses of Lindane and DDE in quarry system during first year.

column samples collected at the same time as the sediment samples was less than the detection limit (30 ng/L) of the analytical technique which was employed.

Model projections for DDE and Lindane are shown in Figure 10. These projections are simply a continuation of the previously presented model calibration with kinetic and transport parameters held constant in time after Day 10. The initial rapid decrease of DDE in the water column during the first year is followed by an exponential rate of decrease over the next 11 years. The sediment concentration time history parallels the water column profile, and at the time of the June 1977 sampling, the calculated sediment concentration is 5.6 μg/L. Considering the simplifying assumptions in the modeling framework, the uncertainty associated with many of the parameter estimates, and the precision of the data, the calculated and observed concentrations at $t = 5$ years are considered to be in excellent agreement. The fact that the calculated and observed water column concentrations are less than the detection limit gives further credence to the modeling analysis. The model results also indicate the projected DDE levels in the quarry sediment 10 years after the original dosing, in June 1982, were approximately 1 μg/L.

Lindane concentrations were not measured at the time of the 1977 sampling. The model projections indicate that the Lindane concentration in the water was eventually reduced to the same concentration as DDE after about five years, while the sediment Lindane concentration was two to three orders of magnitude lower than the sediment DDE concentration at that time. The estimated mass of Lindane remaining in the quarry of 0.014 grams is less than 5% of the mass of DDE in the system at that time (0.330 grams), even though the estimated water column decay rates for DDE were an order of magnitude higher than the decay rates for Lindane. This is especially surprising when one considers that the Lindane concentration in the water column was much higher than the concentration of DDE during the first year, thereby giving the appearance that Lindane was the more persistent chemical. These model results underscore the significance of chemical partitioning on chemical fate and highlight the importance and utility of a modeling framework which incorporates realistic mechanisms of water column and sediment interaction.

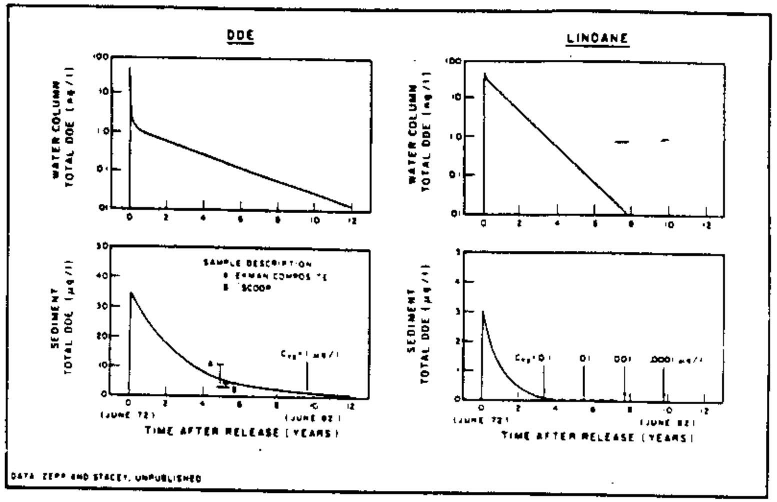


Fig. 10. Long term model verification/projection for Lindane and DDE.

Acknowledgement — This paper is based upon a project conducted by HydroQual for the Chemical Manufacturers Association (CMA). The cooperation and support of our project officer, William P. Gulledge, and past and present members of CMA and the CMA Aquatic Research Task Group: Larry Games, Thomas Neubecker, William Pagano, R. E. Bailey, W. Bishop, J. L. Hamelink, R. A. Kimerle, E. C. Ladd, A. H. Lasday, G. Loewengart, R. J. Moolenaar, C. F. Muska, C. P. Priesing, R. J. Samelson, W. F. Tully, G. V. Cox and R. R. Romano is gratefully acknowledged. The data set used in this analysis, generated under the direction of Jerry Hamelink, was a portion of the doctoral research of Ronald Waybrant. They are to be congratulated for conducting and reporting a well conceived and executed experiment. The members of the North Texas State University research group, Kenneth L. Dickson, J. H. Rodgers and F. Y. Saleh also provided much needed experimental data. Richard Zepp provided timely assistance and the post experiment sediment sampling data. Members of the HydroQual technical staff who have also contributed to this project are John St. John, James J. Fitzpatrick and Michael Kontaxis. We are grateful to all for their assistance.

REFERENCES

1. **Dickson, K.L., A.W. Maki and J. Cairns, Jr.**, eds., 1982. *Modeling the Fate of Chemicals in the Aquatic Environment*. Ann Arbor Science Publications, Ann Arbor, MI.
2. **Waybrant, Ronald**. 1973. Factors controlling the distribution and persistence of Lindane and DDE in lentic environments. Ph.D. thesis. Purdue University. University Microfilms, Ann Arbor, Mich., Order No. 74-15, 256.

3. **Di Toro, D.M., D.J. O'Connor, R.V. Thomann and J.P. St. John.** 1982. Simplified model of the fate of partitioning chemicals in lakes and streams. In K. L. Dickson, A. W. Maki, and J. Cairns, Jr., eds., *Modeling the Fate of Chemicals in the Environment.* Ann Arbor Science Publications, Ann Arbor, MI, pp. 165–190.
4. **HydroQual, Inc.** 1981; 1982. Analysis of Fate of Chemicals in Receiving Waters and Testing of the CMA—HydroQual Model Using Organic Chemical Field Data. Prepared for Chemical Manufacturers Association Aquatic Research Task Group. Mahwah, NJ.
5. **U.S. Environmental Protection Agency.** 1979. Water-related Environmental Fate of 129 Priority Pollutants. Volume I. EPA 440/4-79-029a.
6. **O'Connor, D.J. and J. Connolly.** 1980. The effect of concentration of adsorbing solids on the partition coefficient. *Water Res.* 14:1517–1523.
7. **Dickson, K.L., J.H. Rodgers and F.Y. Saleh** 1981. Measuring rate constants for chemicals in simple model aquatic laboratory systems. Prepared for CMA Aquatic Research Task Group by North Texas State University (NTSU), Denton, TX.
8. **HydroQual, Inc.** 1984. Analysis of Fate of Chemicals in Receiving Waters, Phase IA, Initial Microcosm Data Analysis. Prepared for Chemical Manufacturers Association Aquatic Research Task Group. Mahwah, NJ.
9. **Zepp, R.G. and D.M. Cline.** 1977. Rates of Direct Photolysis in Aquatic Environment. *Environ. Sci. Tech.* 11:359–366.
10. **Singmaster, J.A.** 1975. Environmental Behavior of Hydrophobic Pollutants in Aqueous Solutions. Ph.D. Thesis. University of California at Davis. (As quoted in [5].)