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MODELING POLLUTANTS IN AQUATIC SEDIMENTS

I. ORGANIC POLLUTANTS
II. TOXIC METALS

I. ORGANICS

① Equilibrium Partitioning

$$C_s = K_d C_w \qquad K_d = \frac{C_s^{eq}}{C_w^{eq}}$$

K_d (OR "K_p")

For org. pollutants, mostly due to partitioning to natural organic phase

ANALOGOUS TO OCTANOL ⟷ WATER

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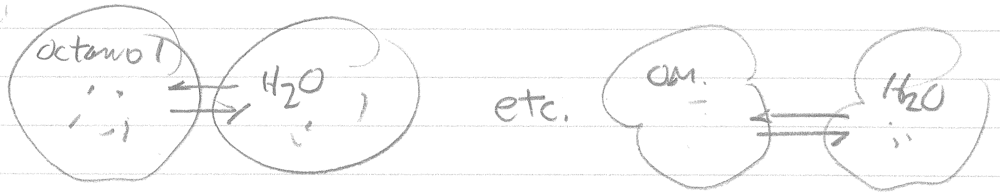
② [SLIDE]



$$K_{OC} = (K_{OM}) = \frac{C_{OC}}{C_w}$$

SAME THING

$$\log K_{OC} \propto \log K_{OW} \quad \text{because} \quad \log K = \frac{-\Delta G^\circ}{2{,}3RT}$$

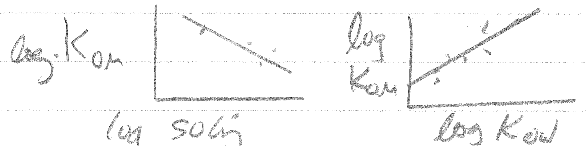
$$\therefore \quad \Delta G^\circ_{OC} \propto \Delta G^\circ_{OW}$$

Free energy of oc Adsorption from water	Free energy of octanol adsorption from water

LINEAR RELATION

Linear
Free
Energy
Relationship
[LFER]

[SLIDE]



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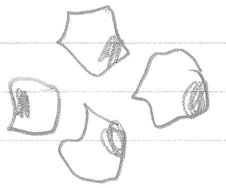
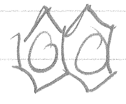
③ REAL SOIL   Say 5% organic content


$\rightleftharpoons H_2O$

$$\boxed{K_d = f_{oc} K_{oc}}$$

Fract. org. carbon

$$K_d = 0.05\,K_{oc}$$

④ Ex: PAH: Naphthalene 

$\log K_{ow} = 3.36$

Use $\log K_{oc} = 0.937 \log K_{ow} - 0.006$ ($r^2 = 0.95$ for PAHs)

$= (0.937)(3.33) - 0.006$

$K_{oc} \simeq 1400 \frac{L}{kg}$

$K_d = f_{oc} K_{oc} = (0.05)(1400) = 70 \frac{L}{kg}$

⑤ Sample Calculations

$\frac{C_s}{C_w} \cong 70 \frac{L}{kg}$ Expect? (Mostly on solid)

So if we have a slurry of sed & water, add
(approx 1:1 solids:liquid)   1 L + 1 kg-solids
Add 100 mg Naphth

Guess $C_s \approx 100$ mg/kg   (~ all goes on sediment)

$C_w = \frac{C_s}{70\, L/kg} = \frac{100\ mg/kg}{70\ L/kg} = 1.4\ mg/L$

Refine $C_s = 98.6$ mg/kg $C_w = \frac{98.6}{70} = 1.4$

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⑥

So, for $K_d \tilde{>} 100 \frac{L}{kg}$ can assume "ALL" ON SOLID PHASE

AS LONG AS "LOTS" OF SOLIDS (as in sediments)

NOTE ⇒ Typical K_{ow}'s (Not K_d)

		$\log K_{ow}$
GAS OLINE	Benzene	2.1
	n-pentane	3.6
PAH	phenanthreen	4.6
	Benzanthracem	5.9
	Arochlor 1260 (PCB)	6.7

Benzene "lightly sorbed"   RANGE

PCB "Super adsorbed"

BUT

⑦

In suspension (Water column) TSS Relatively small

Ex 1 L H_2O + 100 mg sediment

$K_d = 70 \frac{L}{kg}$ Add 100 mg Naphthale

TRY: As above assume 'all' on C_s = 100 mg/100 mg

$$C_s = \frac{100 \text{ mg}}{100 \times 10^{-6} \text{ kg}} = 1 \times 10^{+6} \text{ mg/kg} \quad (!?)$$

$$\frac{C_s}{C_w} = \frac{C_T - C_w}{C_w} = 70 \text{ L/kg}$$

Simpler: Try $C_w \approx \frac{100 \text{ mg}}{L}$ $C_s = \left(70 \frac{L}{kg}\right)\left(100 \frac{mg}{L}\right) = 7000 \frac{mg}{kg}$ ON $100 \text{ mg} = 10^{-4} \text{ kg}$

$$M_s = \left(7000 \frac{mg}{\cancel{kg}}\right)\left(1 \times 10^{-4} \cancel{kg}\right) = \boxed{0.7 \text{ mg}}$$

So refine: $C_w = \frac{100 - 0.7}{\boxed{\approx 99 \frac{mg}{L}}}$ $\boxed{C_s = 6{,}900 \frac{mg}{kg}}$

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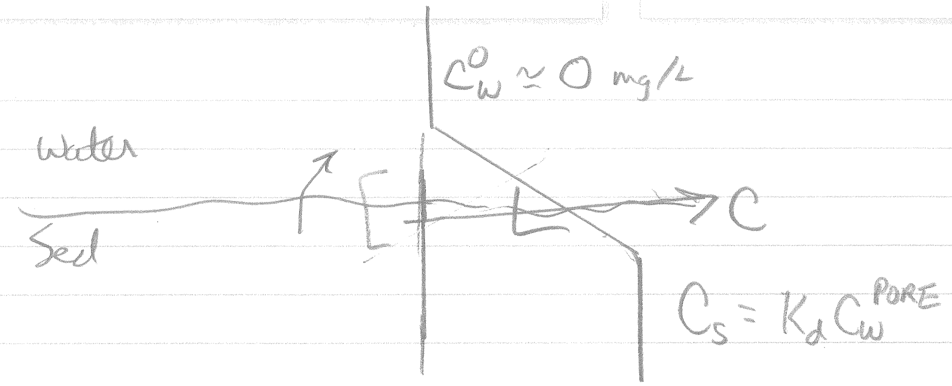
APPLICATIONS

⑧



Diff Flux:

$$J_{sed}^{z} = -D_{pores}\frac{\Delta C}{\Delta Z}$$

ΔC ← $C_w^{PORE} - C_w^{0} \cong C_w^{PORE}$

ΔZ ← ⓘ?

Diffusional layer thickness

$$J_{sed}^{z} = -\left[\frac{D}{\Delta Z}\right]\Delta C$$

$$\left(\frac{L^2}{T}\right)/L = \frac{L}{T}$$ "Piston Velocity"

II. METALS

⑨ Kd ↑ works

Different correlations

"AVS" Concept Acid-Volatile Sulfide

$$H_2S \rightleftharpoons HS^- \rightleftharpoons S^{2-}$$

pKa → 7.0 13.9

Ksp: FeS log K_{sp} = 18.1

MnS ≈ 10.5/13.5

AUS = FeS + MnS (Amorphous; Not PYRITE)

Ni^{2+} = 19.4

Co^{2+} = 21.3

Zn = 24.7

Cd = 27.0

Pb = 27.5

Cu = 36.1

Ag = 50.1

⑩ **AVS:** "NATURAL" FeS + MnS

PLUS Heavy Metal sulfide solids (ZnS, CdS, etc.)

RULES: ① If AVS > SEM^{*}_{TOTAL} (mol/kg)

All SEM concs ≅ 0 mg/L (zero)

② If SEM_{TOT} < AVS (mol/kg)

"Remove" metals ($C_w \cong 0$) in order of least soluble sulfide

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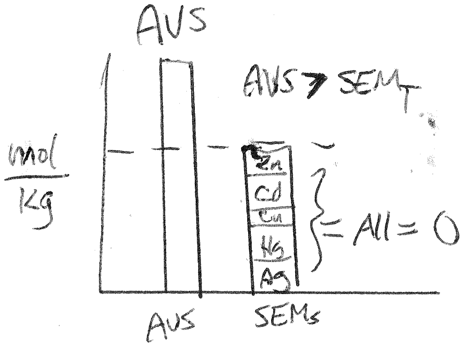
⑪ ANAYSES: ① Measure AVS

a.) Acidify: Dissolves ~all sulfides AND All sulfides → H_2S

b) Strip off VOLATILE H_2S + Measure = AVS (mol/kg-sed)

* ② Take the acid supernatant and measure the "simultaneously extracted metals" OR "SEM" (see above)



CONVERT

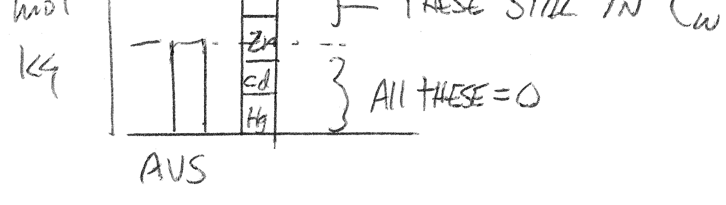
SEMs: Ni = ~ mg/L ⇒ mol/kg-sed

Zn = ~ mg/L ⇒ mol/kg

⋮

Cu = ~ mg/L ⇒ mol/kg

Hg = ~ mg/L ⇒ mol/kg



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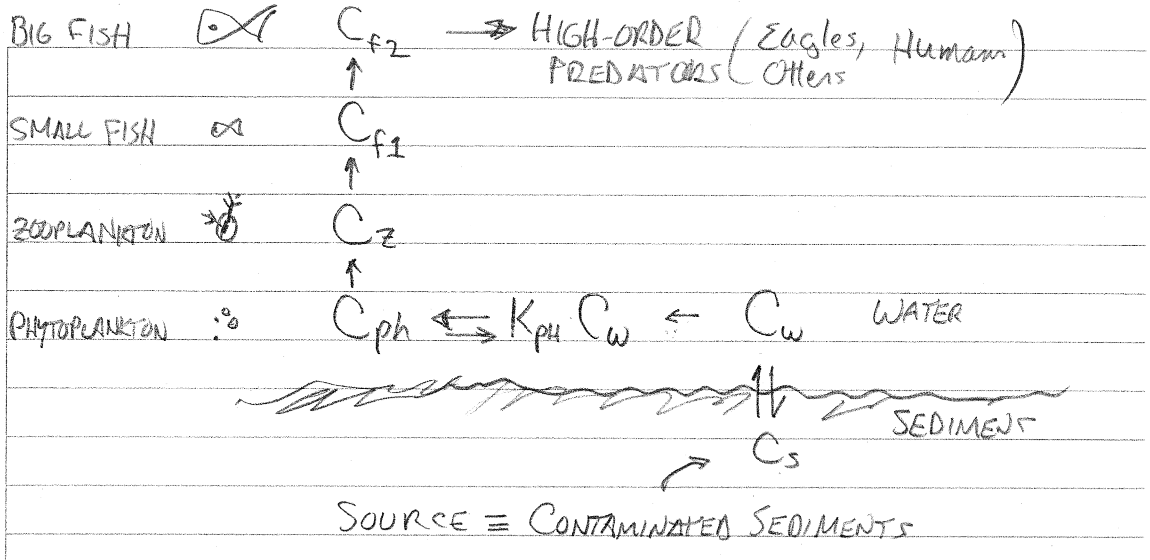
BIOAMPLIFICATION UP TROPHIC LEVELS

①



SOURCE ≡ CONTAMINATED SEDIMENTS

②

In principle, can relate uptake by humans, or eagles, etc as a function of the strength (concentration) of pollutant in sediment

E.g. $C_s \Rightarrow$ HUMAN UPTAKE

[BAF MODEL]

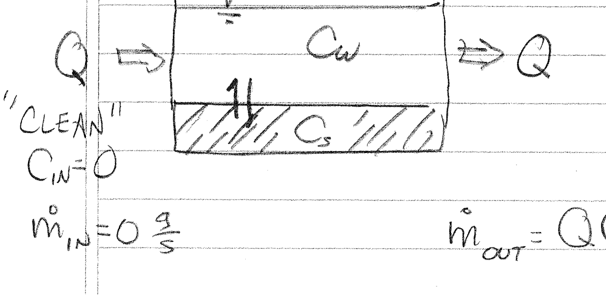
"FORCING FUNCTION" "RESPONSE" (OR RECEPTOR UPTAKE)

③

COMPLICATIONS
- ☐ Food web w/ many links
- ☐ Dynamic food web populations (seasonal or other variations in trophic levels)
- ☐ Other sources besides sediments (groundwater, runoff, atmospheric)

OR,

OUR TOPIC ⇒ RATE AT WHICH CONTAMINANT LEAVES SEDIMENT



$\dot{m}_{OUT} = QC_w$

Imagine lake/pond/river reach

→ Unpolluted water enters

→ Contaminant moves sed → water

→ C_w Results

→ C_w → Enters food chain

QUESTION: WHAT CONTROLS C_w?

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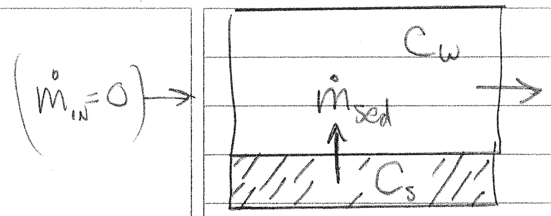
④



$$\rightarrow \dot{m}_{out} = QC_w = \dot{m}_{sed}$$

$$\uparrow fcn(C_s)$$

Several possibilities

1. TRUE EQUILIBRIUM BETWEEN SURFACE WATER C_w AND SEDIMENT CONC, C_s

$$\frac{C_s}{C_w} = K_p \quad \text{or} \quad C_w = \frac{C_s}{K_p} \quad \underline{\text{ALWAYS}}$$

- Flow rate Q does not affect C_w. $\dot{m} = QC_w = Q\frac{C_s}{K_p}$
- C_w & pollutant efflux governed by thermodynamic factor K_p

⑤

2. Suppose Q increases enough so that

$$\underset{\text{MORE LEAVES}}{\dot{m}_{out}} = QC_w > \dot{m}_{sed} \quad \text{THAN ENTERS}$$

Then $\frac{\Delta C_w}{\Delta t} \neq 0$ (is < 0) C_w DROPS ↓ SO NOW $\boxed{C_w \neq \frac{C_s}{K_p}}$

In fact $\boxed{C_w < \frac{C_s}{K_p}}$ or, C_w less than predicted by equilibrium Calc

⑥

CONSEQUENCE? Food chain governed by C_w (as before) BUT C_w no longer just simple proportion of C_s. ∴ Exposure to humans, etc. now depends in part on RATE of contaminant transfer ($\dot{m}_{sed}$).

⇒ So, steady-state possible, but it is a dynamic steady-state, not an equilibrium state

⑦ Now we can rewrite governing eqn for C_w

$\left[C_w \neq \frac{C_s}{K_p}\right]$ $\quad QC_w = \dot{m}_{out} = \dot{m}_{sed}$

$$\boxed{C_w = \frac{\dot{m}_{sed}}{Q}}$$

Now, must evaluate $\dot{m}_{sed}$ transport rate to calc. C_w
Three main possibilities for $\dot{m}$

1. $\dot{m}$ controlled by DIFFUSION OUT OF SEDIMENT
2. $\dot{m}$ controlled by ADVECTION THROUGH SEDIMENT
3. $\dot{m}$ controlled by rate at which sed. RELEASES contaminant

1) & 2) CONSIDERED "TRANSPORT LIMITED" (or macro-scale transport limited)

3) CONSIDERED "CHEMISTRY LIMITED" (or micro-scale transport limited.)

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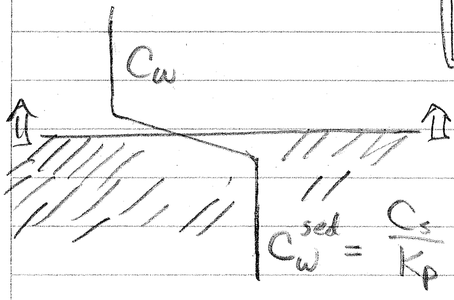
⑧ CASE ①

DIFFUSION LIMITED

$$\boxed{\dot{m}_{sed} = A_s J_z = -A_s D \frac{\partial c}{\partial z}}$$



⇑ LIMITING FLUX J_z USE FICK'S LAW

← Deeper in sediment equilibrium exists between conc. on sed. (C_s) and the POREWATER dissolved C_w^{sed}

$C_w \neq C_w^{sed}$

So $\boxed{C_w = \frac{\dot{m}_{sed}}{Q} = -\frac{A_s}{Q} D \frac{\partial c}{\partial z}}$

Q = vol. flow thru C.V.
A_s = Area of contaminated sediment

⑨ OR/ Empirical mass transfer version: $\left[\frac{D_{eff}}{\Delta z}\right] \equiv k_T$; $\Delta C = C_w - C_w^{sed}$

$C_w = -\frac{A_s}{Q} k_T (C_w - C_w^{sed})$ AND IF $C_w^{sed} \gg C_w$ then simplify

$C_w \cong \frac{A_s}{Q} k_T C_w^{sed} \Rightarrow \boxed{C_w = \frac{A_s}{Q} \frac{k_T}{K_p} C_s}$

(SEDIMENT)

⑩ CASE ②

ADVECTION LIMITED If significant advection of groundwater (or "baseflow") thru the sediment

(Usually will be much greater than diffusion)

$$\boxed{\dot{m}_{sed} = w_{gw} C_w^{sed} A_s} \leftarrow \text{(Adv. FLUX)} \times \text{(AREA)}$$

Porewater concentration

Vertical groundwater velocity (advection) = "Darcy Flux"

Now $C_w = \frac{\dot{m}_{sed}}{Q} = \frac{w_{gw} C_w^{sed} A_s}{Q}$

⑪

And $\left(w_{gw} = Q_{gw}/A_s\right)$ $\left(C_w^{sed} = C_s/K_p\right)$

So can write

$$C_w = \left(\frac{w_{gw} A_s}{Q K_p}\right) C_s$$

OR

$$C_w = \left(\frac{Q_{gw}}{Q}\frac{1}{K_p}\right) C_s$$

⑫ CASE ③

DESORPTION ("CHEMISTRY") LIMITED

Limiting desorption rxn: $C_s \rightarrow C_w^{sed}$

Assume 1st ORDER: $\frac{dC_w^{sed}}{dt} = \frac{\rho_B}{\phi} k_d C_s$ (k_d = 1st order desorption rate constant)

If [diffusion + advection] are "fast enough" and NOT limiting the flux, then mass flux of desorption (limiting flux) is

$$\dot{m}_{sed} = V_s \frac{dC_w^{sed}}{dt} = (A_s d_s)\frac{\rho_B}{\phi} k_d C_s$$

$$\boxed{C_w = \frac{m_{sed}}{Q} = \left(\frac{A_s d_s \rho_B k_d}{Q \phi}\right) C_s}$$

ρ_B = Bulk Density of Sediment (kg_s/L_T)

ϕ = porosity of sed (L_w/L_T)

k_d = 1st order desorption constant

SUMMARY

Q = Bulk flow over sed.

A_s = Area of contaminated sediment

K_p = sed/water partition coeff.

k_T = Diffusional mass transfer coeff. sed → water

Q_{gw} = Total groundwater flow thru sediment (in A_s zone)

d_s = depth of contaminated sed.

k_d = 1st order desorption rate coefficient

ρ_B = bulk density sediment

ϕ = porosity of sediment

NON-EQUILIBRIUM BETWEEN SEDIMENT AND OVERLYING WATER FOR 3 LIMITING CASES, FORMULAE FOR $C_w = fcn(C_s)$

1. DIFFUSION LIMITED

$$C_w = \left(\frac{A_s k_T}{Q K_p}\right) C_s$$

2. THRU-SEDIMENT ADVECTION LIMITED

$$C_w = \left(\frac{Q_{gw}}{Q K_p}\right) C_s$$

3. DESORPTION (CHEMISTRY) LIMITED

$$C_w = \left(\frac{A_s d_s \rho_B k_d}{Q \phi}\right) C_s$$

WHEN IS ADVECTION MORE IMPORTANT THAN DIFFUSION

Find basically a Péclet Number $\left(Pe = \frac{LV}{D} = \frac{\text{Advection}}{\text{Diffusion}}\right)$

$$\frac{C_w^{ADV.}}{C_w^{DIFF}} = \frac{\frac{Q_{gw}}{Q} \frac{1}{K_p}}{\frac{A_s k_T}{Q K_p}} = \frac{Q_{gw}}{A_s k_T}$$

$$\boxed{Pe^{sed} = \frac{w_{GW}}{k_T} = \frac{\text{G/W Advective Velocity}}{\text{Diffusive Piston Velocity}}}$$

For $Pe^{sed} >> 1$ G/W Advection Limits C_w

Fe $Pe^{sed} << 1$ Diffusion Limits C_w

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WHEN IS DESORPTION LIMITING TO ADVECTIVE TRANSPORT?
(I.e., when is advection "faster" than the rate at which contaminant desorbs off sediment?)

Find basically a Damköhler II No.

$$\left(Da_{II} = \frac{\text{Reaction Rate}}{\text{Adv. Mass Transfer Rate}} \right)$$

$$\frac{C_W^{CHEM}}{C_W^{ADV}} = \frac{\dfrac{A_s d_s k_d \rho_B}{\cancel{Q}\,\phi}}{\dfrac{Q_{gw}}{\cancel{Q}\,K_p}}$$

$$= \frac{(A_s d_s \rho_B)\,k_d K_p}{\phi\, Q_{gw}} = \frac{\left(\cancel{V_s} \cdot \dfrac{M_s}{\cancel{V_s}}\right) k_d K_p}{\phi\, Q_{gw}}$$

$$= \frac{(M_s K_p)\,k_d}{\phi\, Q_{gw}} = \frac{\left(\cancel{M_s} \dfrac{V_{Gw}}{\cancel{M_s}}\right) k_d}{\phi\, Q_{gw}} = \frac{V_{gw}\, k_d}{\dfrac{V_{gw}}{\tau_R}\,\phi}$$

$$Da_{II} = \frac{k_d}{\phi / \tau_R} = \frac{\phi\, \tau_R}{k_d} = \frac{\text{Char. RESIDENCE TIME SCALE}}{\text{Char. REACTION TIME SCALE}}$$

SMALL Da → Chem. Desorption LIMITS C_W

LARGE Da → ADVECTION thru SED. LIMITS C_W