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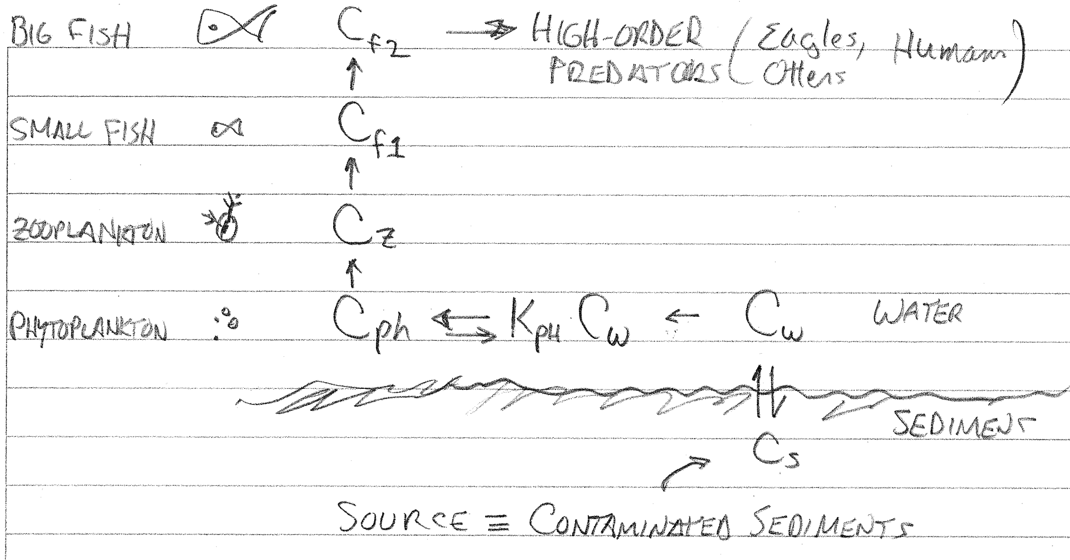
BIOAMPLIFICATION UP TROPHIC LEVELS

①



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)

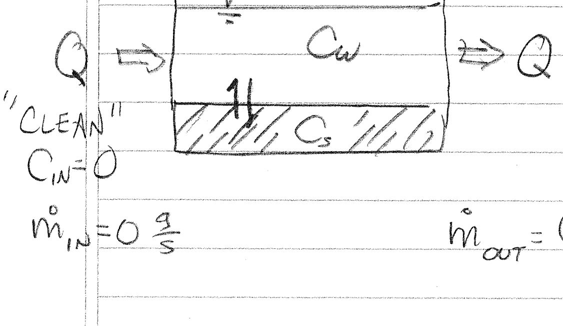
③

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



Imagine lake/pond/river reach

→ Unpolluted water enters

→ Contaminant moves sed → water

→ C_w Results

→ C_w → Enters food chain

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

QUESTION: WHAT CONTROLS C_w?

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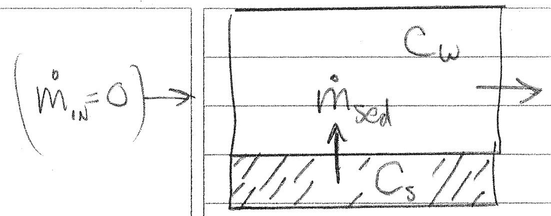
④



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

$\updownarrow$ 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

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

$\uparrow$ MORE THAN ENTERS LEAVES

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.

$\therefore$ 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

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

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

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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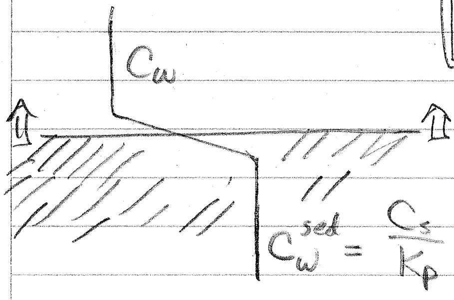
⑧ CASE ① DIFFUSION LIMITED

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



⇑ 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}

$$C_w \neq C_w^{sed}$$

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

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)

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

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)

ρ_B = Bulk Density of Sediment (kg_s/L_T)

ϕ = porosity of sed (L_w/L_T)

k_d = 1st order desorption constant

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

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

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

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

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 ground-water 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

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.

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

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

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

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

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

SMALL Da → Chem. Desorption LIMITS C_W

LARGE Da → ADVECTION thru SED. LIMITS C_W