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"An Equilibrium Model of Organic Chemical Accumulation in Aquatic Food Webs with Sediment Interaction"

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AN EQUILIBRIUM MODEL OF ORGANIC CHEMICAL ACCUMULATION IN AQUATIC FOOD WEBS WITH SEDIMENT INTERACTION

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Abstract – A five-compartment steady-state food-web model is constructed that includes a benthic invertebrate compartment. Four exposure routes are considered in the description of accumulation by benthic animals: ingestion of particulate contaminants associated with (a) sediment organic carbon and (b) overlying phytoplankton and ventilation of free dissolved contaminant in (c) interstitial and (d) overlying water. Normalization of organism lipid-based chemical concentration to sediment organic carbon (the biota sediment factor, BSF) or to overlying water concentration (the bioaccumulation factor, BAF) indicates the significance of the sediment/overlying water partition coefficient for systems that have a benthic component. The impact of the benthic component on a forage fish is related directly to this partitioning. Application of the model to an amphipod-sculpin web for Lake Ontario indicates (a) amphipod water exposure is a combination of interstitial and overlying water concentrations, (b) amphipod feeding appears to be a combination of overlying phytoplankton and sediment organic carbon, (c) amphipod and sculpin chemical assimilation efficiency appears to be a complicated function of octanol-water partition coefficient, (d) observed BAF for amphipod and sculpin is about one order of magnitude higher than log K_{ow} in the range 5.5 to 7.0 and is calculated to be due almost entirely to food-web transfer from the sediment, as opposed to uptake from the water route.

Keywords – Model Sediment Food chain Benthic invertebrates

INTRODUCTION

The purpose of this paper is to present a generic modeling framework for the accumulation of chemicals in aquatic systems that includes interaction with sediment chemical and sediment biota. Concern has been expressed for sediment-mediated transfer of chemicals in producing fish lesions (e.g., Malins et al. [1]) and in possible trophic transfer [2]. The bioavailability of chemicals from sediments is also of concern in establishing sediment quality criteria [3]. A large number of laboratory experiments of chemical uptake from sediments by benthic invertebrates and to a lesser degree by fish have been conducted (e.g. [4–8]). Likewise, field relationships between sediment chemical concentration and aquatic biota have been measured by many investigators (e.g. [5,9–13]).

Bierman [14] has summarized a considerable data base relating sediment concentrations to concentrations in benthic invertebrates and fish. In that work it was concluded that clear relationships were not evident between organic carbon-normalized sediment concentrations and lipid-normalized residues in biota. The analysis of Bierman is, however, based on a simple partitioning between sediment and biota. The model presented in this work is intended to provide a more comprehensive framework for an initial assessment of the bioavailability of contaminated sediment and the potential for trophic transfer.

MODEL STRUCTURE AND EQUATIONS

The compartmental structure of the food web examined in this model is shown in Figure 1. Five interactive biological compartments are considered, together with the particulate and dissolved contaminant concentration in the water column and sediment. In order to provide a generic, tractable analysis across food webs, the system is assumed to be at a steady state. Whereas it is recognized that natural systems are dynamic, suitable averaging of compartment parameters (e.g., growth rates) and calibration data can provide estimates of a steady-state condition. Benthic invertebrates obtain chemical via uptake from a combination of interstitial water and overlying water and direct ingestion of chemical on sediment particles and/or from phy-

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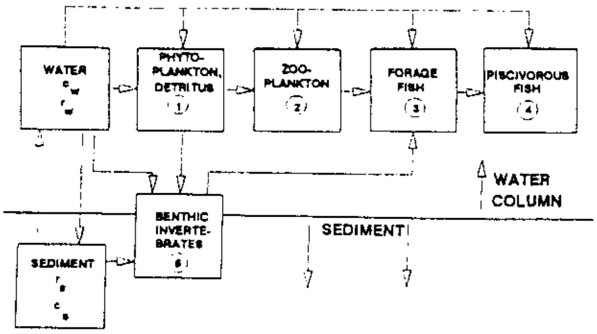


Fig. 1. Schematic of a five-compartment food-web model.

toplankton and detrital material at the sediment-water interface. Forage fish accumulate chemical directly from the overlying water and from food in some linear combination from zooplankton and benthic invertebrates. By allowing the benthic community to interact with both the sediment and the overlying water column, the chemical transfer between the sediment and the overlying water must also be included.

Lipid and organic carbon normalizations

Partitioning of organic chemicals into aquatic organisms is governed to first order by the lipid pool of the organism [15-17]. Also, as noted in a review of sediment water quality criteria [3] and as discussed by Bierman [14], the partitioning of organic chemicals is determined to a large degree by the amount of organic carbon present in the particulate matter. The model equations presented herein are therefore written in terms of chemical concentrations in aquatic organisms on a lipid basis and for abiotic particles on an organic carbon basis.

The tendency for organic chemicals to partition into lipid and organic carbon pools is broadly represented by the octanol/water partition coefficient (K_{ow}). In this work, to first approximation, the preference for chemicals to partition to octanol, lipid, and organic carbon is considered identical.

The chemical concentration in an organism on a lipid basis, ν[μg chemical/kg (lipid)], is related to the wet-weight chemical concentration, ν_{wt}[μg chemical/kg (wet)], and the fraction lipid, f_L[kg (lipid)/kg (wet)], by

$$\nu = \frac{\nu_{wt}}{f_L}. \tag{1}$$

Model equations

The basic model equations are an extension of the equilibrium model of a pelagic food chain given in [17]. For all of the model state variables, let ν_i be the chemical concentration in the ith compartment on a lipid basis [μg/kg (lipid)], c_w and c_s be the freely dissolved chemical concentration [μg/L] in the water column and sediment, respectively, and r_w and r_s be the chemical particulate concentration on an organic carbon basis [μg/kg (org C)] in the water column and sediment, respectively.

The rate of chemical uptake from available dissolved pools is k_{ui} [L/d-g (lipid)]; the specific feeding rate of organism i on j (or on sediment) is $I_{L,i}$[g (prey lipid)/g (predator lipid)-day] or $I_{Loc,5}$ [g(org C ingested)/g (predator lipid)-day]; the chemical assimilation efficiency of ingested chemical is α_{ij} [g chemical assimilated/g chemical ingested]; and the excretion rate is K_i and the growth rate is G_i, both in units [1/day].

The mass balance equation for the chemical in the benthic compartment (5) is given at steady state by

$$\begin{aligned}\frac{d\nu_5}{dt} = 0 = &[k_{u5}(b_{5s}c_s + b_{5w}c_w)]\\ &+ [(p_{5s}\alpha_{5s}I_{Loc,5})r_s + (p_{51}\alpha_{51}I_{L,5})\nu_1]\\ &- [(K_5 + G_5)\nu_5].\end{aligned} \tag{2}$$

The first bracketed term on the right-hand side of this equation represents the uptake of available chemical by benthic organisms from the sediment interstitial water and the overlying water column, where b_{5s} and b_{5w} are the fraction of uptake from sediment and overlying water, respectively, ($b_{5s} + b_{5w} = 1$). The second bracketed term represents the uptake of chemical from ingestion of sediment [r_s; μg/kg (org C)] and phytoplankton (ν_1), where p_{5s} and p_{51} are the preference for sediment and phytoplankton, respectively ($p_{5s} + p_{51} = 1$). The third term is the loss of chemical due to excretion (K_5) and growth (G_5).

For the phytoplankton/detritus compartment (1), a simple partitioning is used:

$$\frac{d\nu_1}{dt} = 0 = k_{u1}c_w - (K_1 + G_1)\nu_1 \tag{3}$$

where G_1 is the net growth rate of the total phytoplankton biomass.

2.

The equation for the zooplankton compartment (2) is given by

$$\frac{d\nu_2}{dt} = 0 = k_{u2}c_w + \alpha_{21}I_{L,2}\nu_1 - (K_2 + G_2)\nu_2. \quad (4)$$

For the forage fish compartment (3), the model equation is given by

$$\frac{d\nu_3}{dt} = 0 = k_{u3}c_w + p_{32}\alpha_{32}I_{L,3}\nu_2 + p_{35}\alpha_{35}I_{L,3}\nu_5 - (K_3 + G_3)\nu_3. \quad (5)$$

In this equation, p_{35} and p_{32} represent the relative feeding preference of forage fish for benthic invertebrates and zooplankton, respectively ($p_{35} + p_{32} = 1$). Note that if $p_{35} = 1.0$, then this compartment represents a fish feeding only on the benthic community.

The piscivorous fish equation is given by

$$\frac{d\nu_4}{dt} = 0 = k_{u4}c_w + \alpha_{43}I_{43}\nu_3 + (K_4 + G_4)\nu_4. \quad (6)$$

Parameter estimation

The preceding model framework contains two broad classes of parameters: those associated with the specific chemical (i.e., uptake and excretion rates and chemical assimilation efficiency) and those associated with organism physiology and behavior (e.g., growth and respiration rates, feeding preferences). The strategy for parameter determination is twofold: estimates of some parameters are obtained from other independent studies in the literature, and estimates of feeding parameters are obtained from sensitivity analyses of the model to calibration data.

The chemical uptake rate is related to the respiration rate of the organism and efficiency of transfer to the chemical across the organism membrane. One expression is given by (see, e.g., Connolly [18])

$$k_{ui} = \frac{a_{oxc}a_c\rho}{a_{wd}f_Lc_{O_2}}\beta \quad (7)$$

where a_{oxc} is the oxygen-to-carbon ratio, a_c is the carbon-to-dry-weight ratio, a_{wd} is the wet-to-dry ratio, β is the ratio of chemical mass transfer coefficient to oxygen mass transfer coefficient, ρ is the organism oxygen respiration rate [g (wet)/g (wet)-day], and c_{O_2} is the oxygen concentration (mg/L). The ratio of the mass transfer coefficients is equal to the ratio of chemical transfer efficiency (E_c) to oxygen transfer efficiency (E_o) when the body burden is zero. E_c has been shown to be a function of K_{ow} (e.g., McKim et al. [19]), with E_c declining at high K_{ow} (≥ 6).

The excretion rate is given by

$$K = \frac{k_u[E_c(K_{ow}), \rho]}{K_{ow}} + K_1 \quad (8)$$

where K_1 represents other losses of chemical due to, for example, fecal loss and metabolism.

The chemical assimilation efficiency is also an apparent function of K_{ow}. A summary of some data for fish is shown in Figure 2. The scatter in the data is large but there is a clear decline in α for log K_{ow} greater than about 6.5.

The above equations for chemical accumulation are related to the bioenergetics of the organism via growth, feeding, and respiration rates. Norstrom et al. [20] and Connolly [18] discuss organism energetics for use in chemical accumulation models.

The energy usage rate P_i [cal/g (wet)-day], as given by Connolly [18], is

$$P_i = \lambda_i(\rho_i + G_i) \quad (9)$$

for growth rate, G in [g (wet)/g (wet)-day] and λ_i in [cal/g (wet)$_i$]. The energy intake rate by the animal is then the energy usage rate divided by the fraction of ingested energy that is assimilated, designated as a. The food consumption rate, I_i, in [g (wet)$_i$/g (wet)$_{i-1}$-day] is then given by

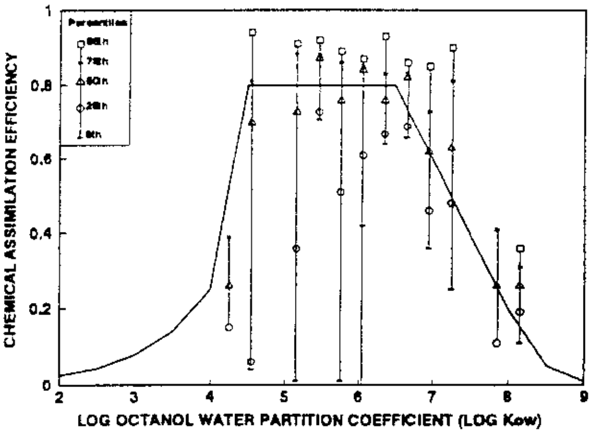


Fig. 2. Variation of chemical assimilation efficiency for fish from 173 references. Solid line indicates relationship used for E_c and α.

$$I_i = \frac{\lambda_i}{\lambda_{i-1}}\,\frac{\rho_i + G_i}{a} \tag{10}$$

for λ_{i-1} as the caloric density [cal/g $(\text{wet})_{i-1}$] of the food. Connolly [18] assumes differences in caloric density to be related to the wet weight–to–dry weight ratio, that is, the caloric density of dry tissue is assumed to be the same for predator and prey. Therefore, the lipid-specific consumption rate for use in Equation 10 is given by

$$I_{L,i} = \frac{(G + \rho)}{a}\left(\frac{a_{wd,i-1}}{a_{wd,i}}\right)\left(\frac{f_{L,i-1}}{f_{L,i}}\right) \tag{11}$$

where $a_{wd,i}$ and $a_{wd,i-1}$ are the wet- to dry-weight ratios for predator and prey, respectively. For organisms feeding on sediment organic carbon,

$$I_{Loc,i} = \frac{G + \rho}{a \cdot a_{wd,i}}\left(\frac{f_{oc,i}}{f_{L,i}}\right) \tag{12}$$

where $I_{Loc,i}$ is in g (org C) ingested/g $(\text{lipid})_i$-day and f_{oci} is the fraction organic carbon of the predator. Equation 12 assumes an approximate equivalence between the caloric density of the benthic animal on a dry-weight basis and the caloric density of the ingested sediment organic carbon. Based on the extensive computation of caloric densities reported by Cummins and Wuycheck [21], this approximation appears to be accurate within a factor of less than two.

For application to data, growth and respiration rates may be assigned through allometric relationships as given in Thomann [17]. In the calibrations discussed below, feeding preferences and sediment exposure were assigned from comparisons to observed data.

Normalization to sediment and overlying water concentration

In order to provide a generic modeling framework, a normalization may be carried out either to the sediment concentration or to the overlying water concentration. The purpose of either approach is to eliminate site specificity. However, as will be seen below, this is possible only under certain assumptions. Let

$$S_i = \frac{\nu_i}{r_s} \tag{13a}$$

be the ratio of the organism chemical concentration on a lipid basis to the sediment chemical concentration on a carbon basis, with units μg/kg (lipid) ÷ μg/kg (org C) or kg (org C)/kg (lipid). This ratio has been termed the biota sediment factor (BSF), (T. F. Parkerton, manuscript in preparation). Similarly, let

$$N_i = \frac{\nu_i}{c_w} \tag{13b}$$

be the ratio of the organism chemical concentration to the free dissolved concentration in the water column, with units μg/kg (lipid) ÷ μg/L or L/kg (lipid). This ratio is the bioaccumulation factor (BAF). Also, let

$$N_{iw} = \frac{k_{ui}}{K_i + G_i} = \frac{\nu_{wi}}{c_w}, \quad i = 1..5 \tag{13c}$$

$$\pi_s = \frac{r_s}{c_s} \tag{13d}$$

$$\pi_{ws} = \frac{r_s}{c_w} \tag{13e}$$

where ν_{wi} is the concentration due to water exposure only.

Equation 13c is the lipid-normalized bioconcentration factor (BCF). Equation 13d is the sediment partition coefficient, that is, the ratio of the sediment chemical concentration (organic carbon basis) to the interstitial freely dissolved chemical concentration. Equation 13e is the partitioning between the sediment chemical concentration and the overlying-water freely dissolved concentration. Note also that

$$N_i = \pi_{ws} S_i. \tag{14}$$

The BSF for the benthic compartment (S_5) is given from Equation 2 as

$$S_5 = \frac{\nu_5}{r_s} = \frac{N_{5w}}{\pi'} + g_{5s} + g_{51}\frac{N_{1w}}{\pi_{ws}} \tag{15}$$

where

$$\pi' = \frac{\pi_s \pi_{ws}}{b_{5s}\pi_{ws} + b_{5w}\pi_s} \tag{15a}$$

and

$$g_{5s} = \frac{p_{5s}\alpha_{5s}I_{\mathrm{Loc.5}}}{K_5 + G_5} \tag{15b}$$

and

$$g_{51} = \frac{p_{51}\alpha_{51}I_{\mathrm{L.5}}}{K_5 + G_5}. \tag{15c}$$

The first term on the right-hand side of Equation 15 represents the uptake of chemical from the water phase of either sediment interstitial water or overlying water. The second term is the chemical accumulation due to consumption of sediment organic carbon. The third term represents the accumulation due to consumption of overlying phytoplankton. It can be noted that the BSF in general is a complicated function of sediment and overlying-water dissolved and particulate chemical concentration; feeding rates and preferences; and the usual uptake, excretion, and growth rates.

The BSFs for the remaining trophic levels are

Phytoplankton: $$S_1 = \frac{\nu_1}{r_s} = \frac{N_{2w}}{\pi_{ws}} \tag{16}$$

Zooplankton: $$S_2 = \frac{\nu_2}{r_s} = \frac{N_{2w}}{\pi_{ws}} + g_{21}S_1 \tag{17}$$

Forage fish: $$S_3 = \frac{\nu_3}{r_s} = \frac{N_{3w}}{\pi_{ws}} + g_{32}S_2 + g_{35}S_5 \tag{18}$$

Piscivorous fish: $$S_4 = \frac{\nu_4}{r_s} = \frac{N_{4w}}{\pi_{ws}} + g_{43}S_3 \tag{19}$$

where for all compartments

$$g_{ij} = \frac{p_{ij}\alpha_{ij}I_{\mathrm{L},i}}{K_i + G_i}. \tag{19a}$$

This latter quantity (and Eqns. 15b and c) represents the food-chain multiplier and is a measure of the extent to which dietary exposure contributes to the total BSF. In Equations 15 through 19, the interaction of organism exposure to sediment water or overlying water is given by π_{ws}.

The BSF normalization for forage and top predator fish for water uptake depends only on the π_{ws} partitioning. This is a disadvantage because π_{ws} is site specific. However, if the contribution from the water phase is small, then the effect of site specificity is lessened. Also, sediment data are often more frequently available than water column data but tend to be more heterogeneous than water column data.

The BAF equation for the benthic compartment is given by

$$N_5 = \frac{\nu_5}{c_w} = N_{1w}\left[\frac{\pi_{ws}}{\pi'}\right] + g_{5s}\pi_{ws} + g_{51}N_{1w}. \tag{20}$$

Note that for uptake from water only, the BAF for the benthic invertebrate is the BCF corrected by the relationship between sediment and overlying water (π_{ws}) and the relative water exposure route (π'). If the benthic invertebrates are exposed entirely to the overlying water ($b_{5w} = 1.0$), then π_{ws}/π' is unity.

The BAF for the forage fish (compartment 3) with consumption of benthic organisms is given by

$$\begin{aligned} N_3 = \frac{\nu_3}{c_w} &= N_{3w} + g_{32}N_2 + g_{35}N_5 \\ &= \{\mathrm{N}_{3w} + g_{32}(N_{2w} + g_{21}N_{1w})\} \\ &\quad + \left\{g_{35}\left[N_{5w}\left(b_{5s}\frac{\pi_{ws}}{\pi_s} + b_{5w}\right)\right.\right. \\ &\quad \left.\left. + g_{5s}\pi_{ws} + g_{51}N_{1w}\right]\right\}. \end{aligned} \tag{21}$$

As seen, the first group of terms in braces in Equation 21 is the BAF from a three-step food chain. The second term in braces is the accumulation due to consumption of benthic organisms.

Insight can be gained into the preceding equations by considering the following approximations. Let

$$\pi_s \approx K_{ow} \tag{22a}$$

$$N_{1w} \approx K_{ow}. \tag{22b}$$

Equation 22a assumes that the sediment partition coefficient (on an organic carbon basis) is equivalent to the octanol/water partition coefficient, K_{ow} (i.e., 1 L organic carbon is approximately equivalent to 1 L octanol). Equation 22b assumes that growth effects are small and that the lipid-normalized phytoplankton BCF is also equal to the octanol/water partitioning coefficient (i.e.,

5.

1 kg lipid is approximately equivalent to 1 kg octanol). Consider the benthic invertebrate compartment and assume all exposure is attributed to the sediment. Then, b_{5s} and $p_{5s} = 1.0$ and

$$S_5 \approx 1 + g_{5s}. \tag{23}$$

Thus, if the sediment magnification factor, g_{5s}, is small, the ratio of organism to sediment chemical concentration will be approximately unity, indicating no significant biomagnification from the sediment. Then Equation 23 reduces to simple equilibrium partitioning between benthic organism lipid chemical and sediment organic carbon–normalized chemical, as previously hypothesized by McFarland [22], Lake et al. [23], and Bierman [14].

Insight into the forage fish BAF can be gained by approximating Equation 21, using Equation 22 and considering the forage fish to feed only on the benthic invertebrates ($g_{32} = 0$) and the benthic invertebrates to be feeding on and exposed only to the sediment ($b_{5w} = 0$; $g_{51} = 0$). The result is

$$N_3 \approx K_{ow} + (g_{35} + g_{35}g_{5s})\pi_{ws}. \tag{24}$$

The effect of the sediment interaction is now clearer. The BAF is elevated above the approximate equilibrium level of K_{ow} by the magnitude of π_{ws} and the food-chain effects. Equation 24 can be contrasted to a forage fish feeding exclusively in a pelagic chain. Thus

$$N_3 = K_{ow} + (g_{32} + g_{32}g_{21})K_{ow}. \tag{25}$$

Assuming the food-chain multipliers are approximately similar, the impact of the sediment is the ratio of π_{ws} to K_{ow}.

Sediment–water column interaction

The preceding equations for the BSF and BAF include the interaction between the water column and sediment. The ratio π_{ws} (Eqn. 13e) emerges when the benthic invertebrates are feeding on both sediment organic carbon and the carbon of overlying detritus or phytoplankton, or ventilating pore water or overlying water. The partitioning between the sediment and water column may be expressed in terms of the water column partition coefficient, π_w [L/kg (lipid)], given by

$$\pi_w = r_w/c_w \tag{26}$$

and the ratio of particulate chemical in the water and sediment, that is,

$$\pi_{w_s} = \frac{r_s}{r_w}\,\pi_w. \tag{27}$$

The water column partition coefficient can be calculated by using the formulation of Di Toro [24], which incorporates a "solids concentration effect" and is given by

$$\pi_w = \frac{K_{ow}}{1 + f_{ocw}K_{ow}m_w/1.4} \tag{28}$$

where m_w is the water column suspended solids concentration [kg/L] and f_{ocw} is the fraction organic carbon of the water column particulates.

The ratio of particulate chemical in the water and sediment will depend on differences in partitioning and decay between the regions and on whether the system is accumulating or depurating chemical. At steady state this ratio may be expressed as (Di Toro et al. [25])

$$\frac{r_{sd}}{r_{wd}} = \delta \tag{29}$$

where

$$\delta = \frac{(v_u + v_d)f_{ps} + (\pi_s/\pi_w)K_f f_{ds}/\phi_s}{(v_u + v_d)f_{ps} + K_f f_{ds}/\phi_s + k_{ds}H_s} \tag{29a}$$

and v_u and v_d are the resuspension and net deposition velocities (cm/yr), respectively; f_{ps} and f_{ds} are the fraction of chemical in particulate and dissolved form, respectively; K_f is the interstitial diffusion rate (cm/d); ϕ_s is the sediment porosity; and k_{ds} is the sediment decay rate (day^{-1}) for r_{sd} and r_{wd} on a dry-weight basis. Converting to organic carbon basis for the sediment gives

$$\pi_{ws} = \frac{\delta f_{ocw}\pi_w}{f_{ocs}} \tag{30}$$

where f_{ocs} is the fraction organic carbon in the sediment. These relationships are then used to calculate the ratio of sediment particulate concentration to overlying-water dissolved concentration.

CALIBRATION/SENSITIVITY ANALYSIS OF MODEL TO LAKE ONTARIO

Data from Oliver and Charlton [26] for the Niagara River region of Lake Ontario and Oliver and Niimi [9] for the open Lake Ontario are used

6.

Table 1. Parameters used for calibration of sediment-water column partitioning, r_s/c_w, for Lake Ontario

Parameter	Units	Value
f_{ocw}	$[g(OC)/g(d)]_{water\ column}$	0.2
f_{ocs}	$[g(OC)/g(d)]_{sediment}$	0.04
m_w	$(mg\ solids/L)_{water\ column}$	1.0
m_s	$(mg\ solids/L)_{sediment}$	$5.2 \cdot 10^5$
ϕ_s	$L_{water}/L_{water+sed}$	0.8
K_f	cm/d	1.0
v_d	cm/yr	0.1
v_u	cm/yr	0.3
k_{ds}	day^{-1}	0.0

to calibrate the sediment-water interaction ratio. The values shown in Table 1 are considered representative of Lake Ontario. Phytoplankton chlorophyll levels were estimated at 4 μg/L, which for a carbon:chlorophyll ratio of 50 and 40% carbon-to-dry-weight ratio gives a suspended solids concentration of 0.5 mg/L. An additional 0.5 mg/L solids was assumed to represent the inorganic fraction. Figure 3 shows the resulting comparison of the preceding water column and sediment partitioning expressions to the observed data. Figure 3a shows the water column partition coefficient, π_w, as calculated from Equation 28. The sediment-water column partition coefficient, π_{ws}, as calculated from Equation 30 is compared to data in Figure 3b. The difference in this plot between the observed data and the calculated steady-state π_{ws} may be attributed to the non-steady state of the sediment with respect to the water column and indicates that the system is depurating chemical.

The plateau in both π_w and π_{ws} is due to the dependence on the suspended solids concentration. Also, it is seen that π_{ws} exceeds K_{ow} by more than an order of magnitude in the region of log K_{ow} from 3 to 6. Inspection of the BSF equations (i.e., Eqns. 15–19) indicates that at high π_{ws} relative to K_{ow}, the sediment route will tend to be more significant than the water column route.

Data from Oliver and Niimi [9] are used for model calibration in an amphipod–sculpin food web. Table 2 summarizes the organism parameters. Uptake efficiency (E_c) and chemical assimilation efficiency (α) were assumed to have the same straight-line relationships as shown in Figure 2. Feeding preferences and relative sediment exposure are determined from a calibration/sensitivity analysis to the data. Recognizing that the organic suspended solids in the water column are comprised primarily of phytoplankton, the BCF for this first compartment was assigned as equal to π_w, as shown in Figure 3a.

Figure 4a shows results for amphipods ventilating interstitial water only ($b_{5s} = 1$) and feeding only on the sediment ($p_{5s} = 1.0$), and for two cases of chemical assimilation efficiency. As seen, the observed BSF values below 1.0 for K_{ow} (<5) are not captured by the calculation, which generally exceeds the data. Also invoking a constant α (chemical assimilation efficiency) fails to reproduce the decline in BSF at $K_{ow} \geq 7.0$. Figure 4b shows the sensitivity for the amphipods exposed to overlying water only ($b_{5w} = 1.0$) and two feeding assumptions; curve A indicates results when amphipods

Table 2. Model parameters for food-web pelagic/sediment model

Compartment no.	Weight [g (wet)]	f_{Li} (% lipid)	a food assim eff[a]	a_{wdi}	G growth rate[b] (d^{-1})	r respiration rate[c] (d^{-1})	$I_{L,i}$ specific consumption[d]
1[e]	–	1	–	10	–	–	–
2	0.01	5	0.30	5	0.025	0.090	0.154
3	100	8	0.80	4	0.004	0.014	0.016
4	1,000	20	0.80	4	0.0025	0.0090	0.0058
5	0.002	3	0.20	7	0.035	0.125	~~0.186~~ 0.381 1.52[f]

[a] g $(org\ C)_{assim}$/g $(org\ C)_{ingested}$.

[b] $G = 0.01\ w^{-0.2}$, w = g(wet) of organism.

[c] $r = 0.036\ w^{-0.2}$.

[d] Equation 11: g (lipid)/g (lipid)-day.

[e] Compartment 1 is phytoplankton, BCF = Equation 27.

[f] Equation 12: g (org C)/g (lipid)-day.

7.

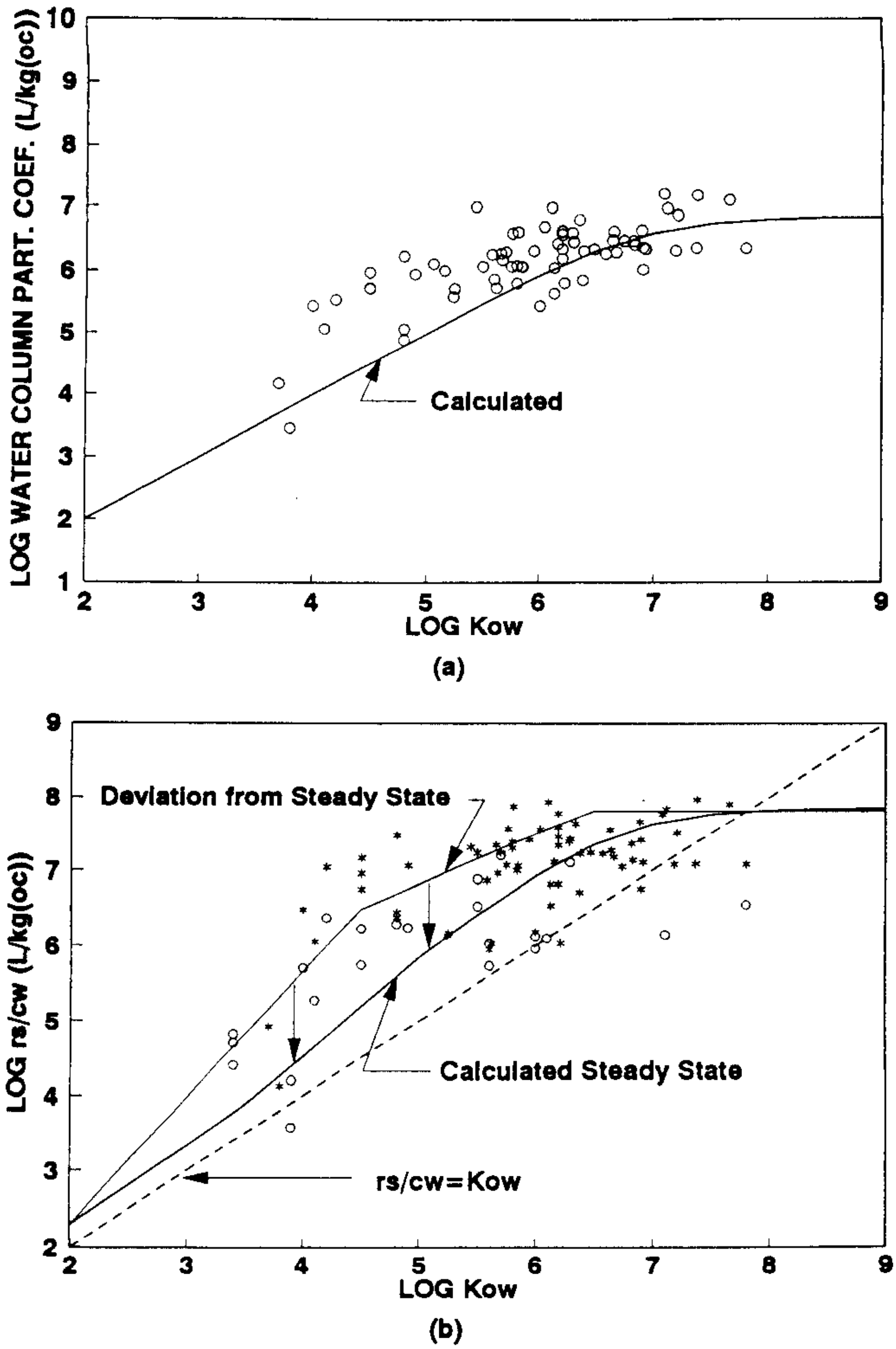


Fig. 3. (**a**) Calculated water column partition coefficient, π_w (Eq. 28) compared to data of Oliver and Niimi [9]. (**b**) Calculated variation of π_{ws} with K_{ow} using Equation 30 and comparison to observed data for Lake Ontario. Stars from [9], open circles from [27].

are assumed to feed exclusively on the sediment ($p_{5s} = 1.0$ in Eq. 2). Curve B assumes an exclusive phytoplankton diet ($p_{51} = 1.0$ in Eq. 2). As seen, the data appear to reflect some combination of feeding on sediment and overlying-water particulates as well as exposure to interstitial and overlying water.

Following analyses of combinations of feeding

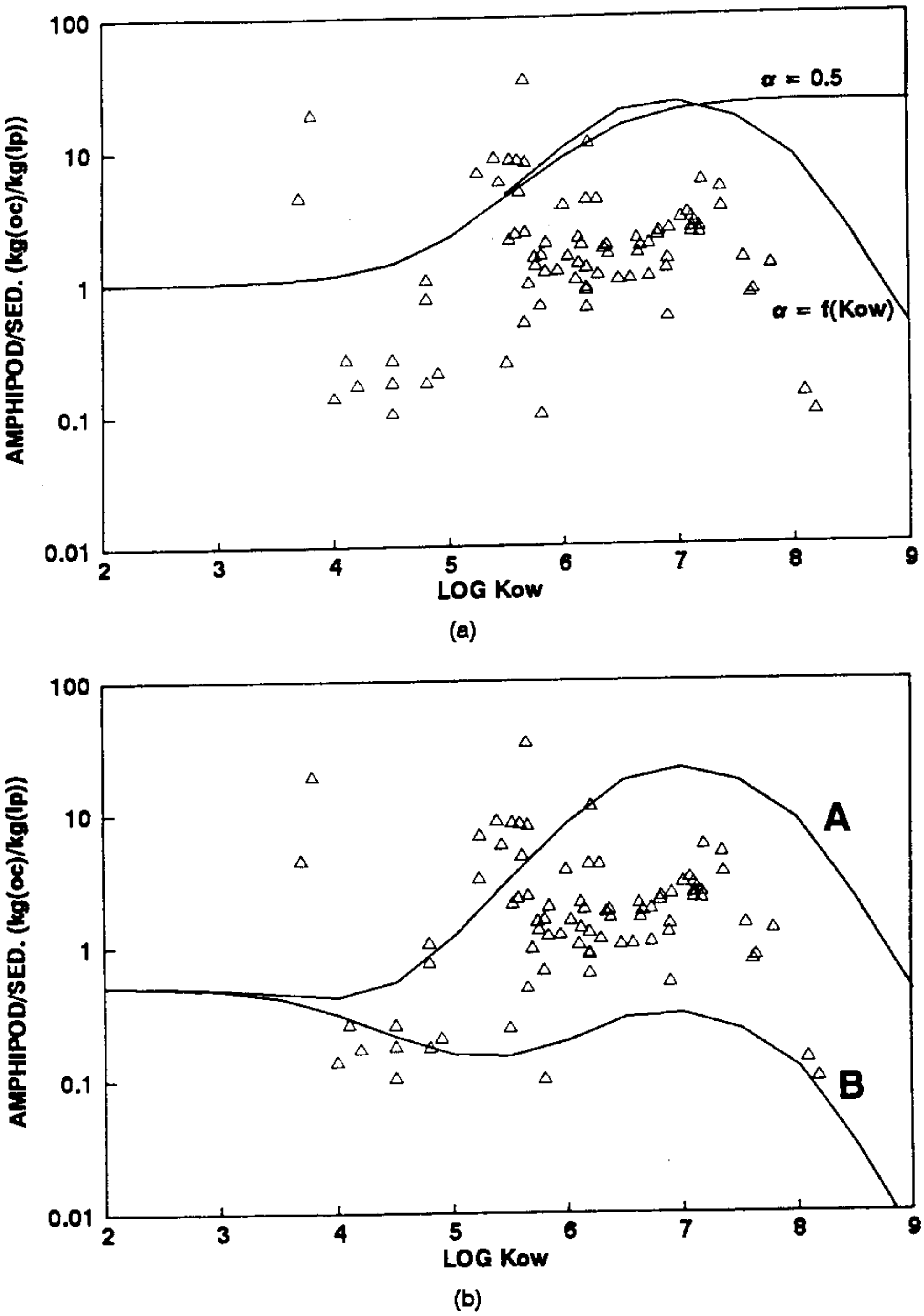
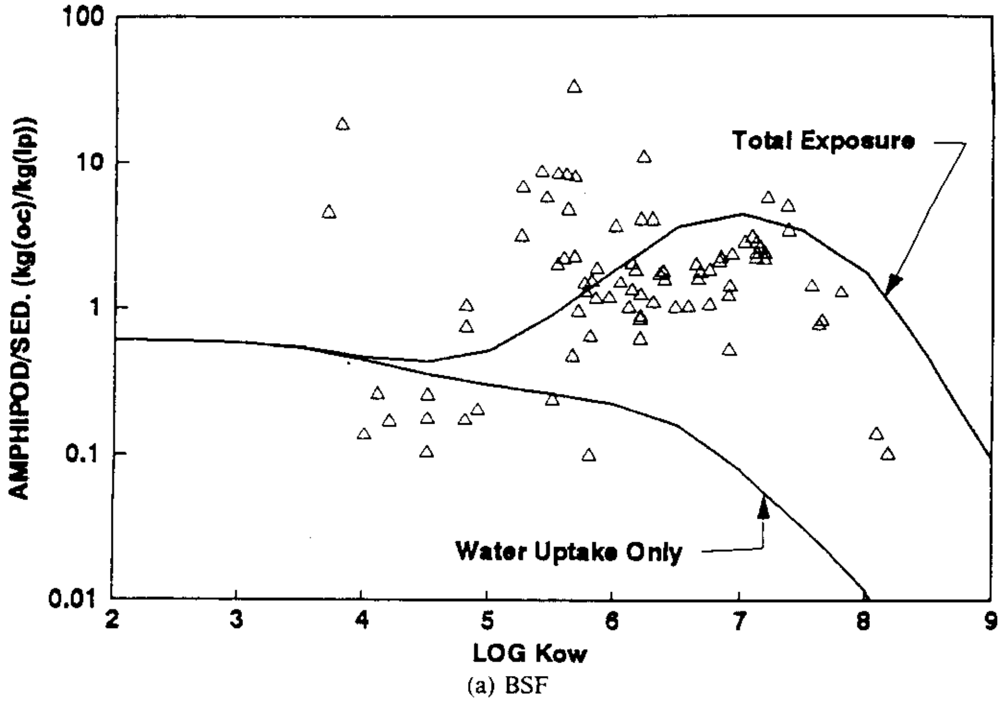
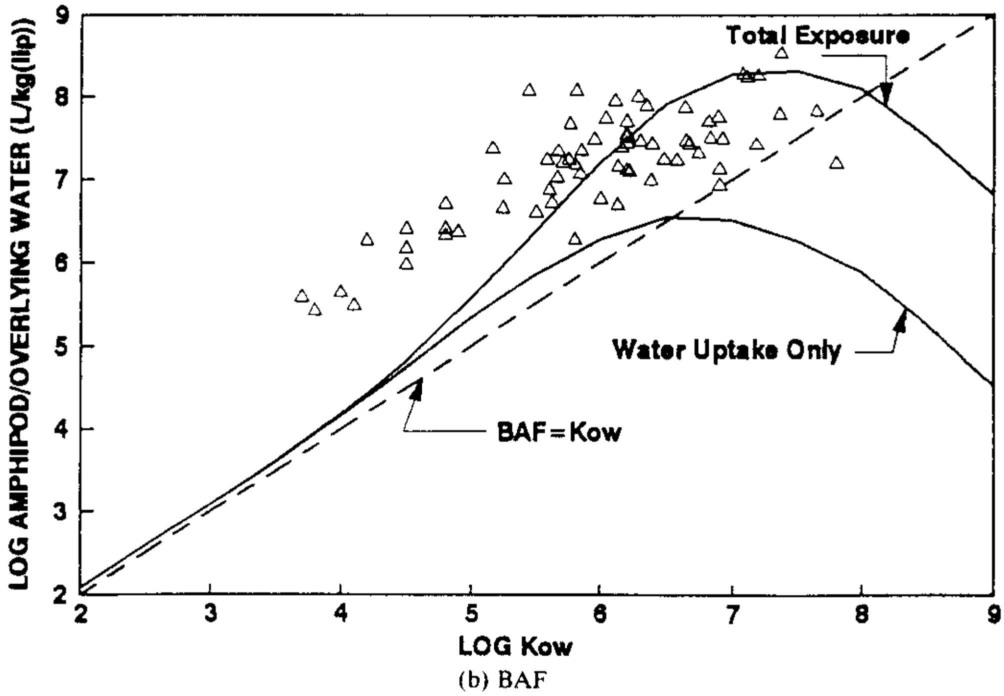


Fig. 4. Comparison of observed data of Oliver and Niimi [9] to amphipod BSF model under different conditions of (**a**) chemical assimilation efficiency and (**b**) water exposure and feeding preference, "A" sediment only, "B" phytoplankton only.

and water exposure, Figure 5a shows the results of a 20% exposure of the benthic invertebrates to the interstitial water, an 80% exposure to overlying water, and a 20% consumption of sediment particulate organic carbon. These combinations are not necessarily unique, and other relationships between exposure and feeding may provide an equally credible representation of the observed data. The model with these assumptions generally represents the data, except in the region of log $K_{ow} > 7.5$. Presumably, the chemical assimilation efficiency drops more rapidly at high K_{ow} than that used in the



(a) BSF



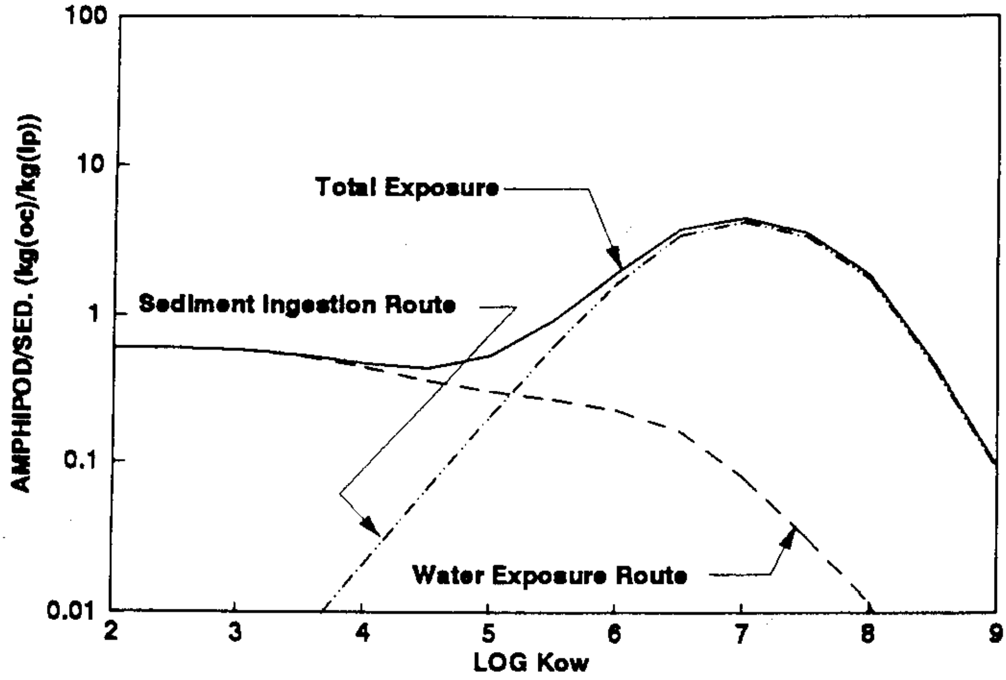
(b) BAF

Fig. 5. Comparison of (**a**) BSF and (**b**) BAF data of Oliver and Niimi [9] to model after calibration using parameters of Table 2, steady-state sediment-water column interaction of Figure 3, 20% ventilation of sediment interstitial water, and 20% consumption of sediment organic carbon.

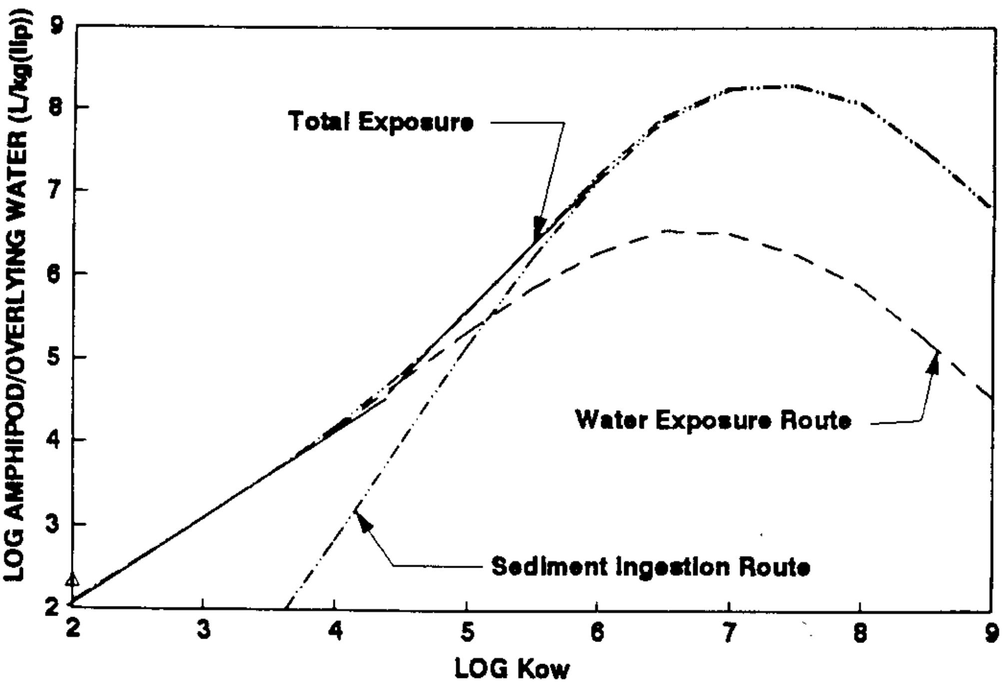
model. The two outlying data points of log $K_{ow} \approx 3.5$ are consistent with the model if the amphipods were from locations of low π_{ws}, which increases the BSF above 1 in this K_{ow} region.

Figure 5b shows the calculated (Eq. 20) and the observed amphipod BAFs. The deviation of calculated BAF from observed data for log $K_{ow} \leq 5$ is attributed to the use of a steady-state π_{ws}. Both

10.



(a) BSF



(b) BAF

Fig. 6. Calculated contribution from the sediment ingestion and water exposure routes to amphipod (a) BSF and (b) BAF.

plots show the contribution of water-only exposure to the BSF and BAF. As seen, the results indicate a significant accumulation due to food consumption above that of water only. Figure 6 shows the relative contribution to the BSF and BAF from the sediment route. As indicated, almost all of the difference between the water and the total BSF and BAF is due to the uptake of contaminated sediment, with very little due to consumption of overlying phytoplankton. This appears counterintuitive because the amphipods are calculated with only a 20% consumption of sediment carbon. Figure 7 shows the explanation.

The three routes shown in Figure 7 are calculated from Equation 15. The water route is N_{5w}/π', the sediment route is g_{5s}, and the phytoplankton route is N_{1w}/π_{ws}. Although amphipod feeding is at 80% of phytoplankton, the relative chemical contribution from this food source is low due to the high π_{ws}. That is, the amphipod BSF is reduced by not feeding entirely on the sediment, but its body burden is still due almost entirely to the sediment.

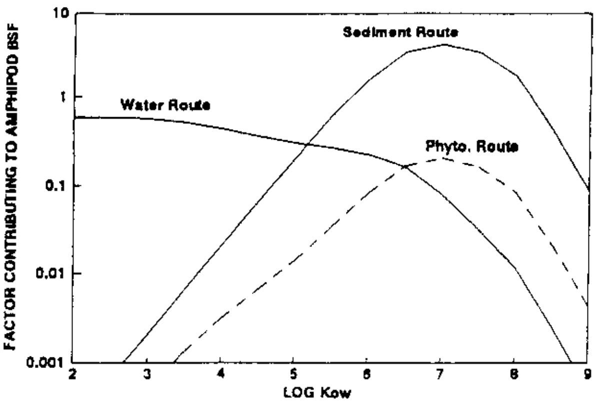
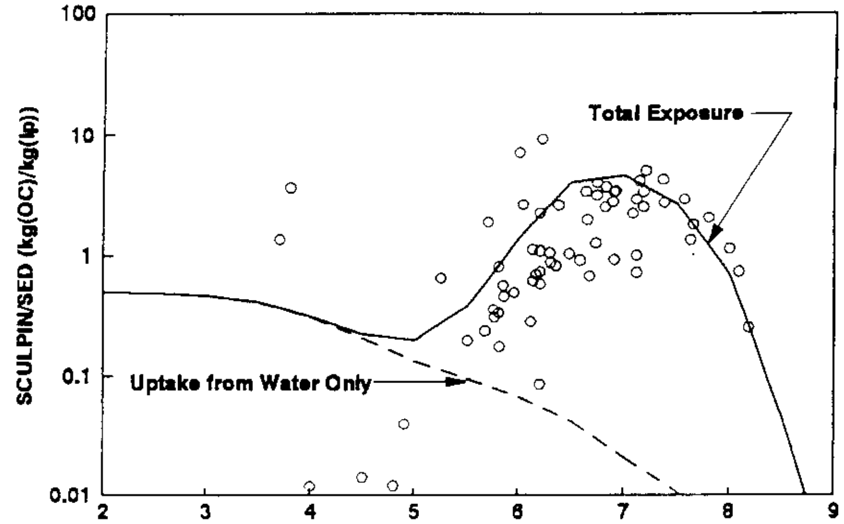
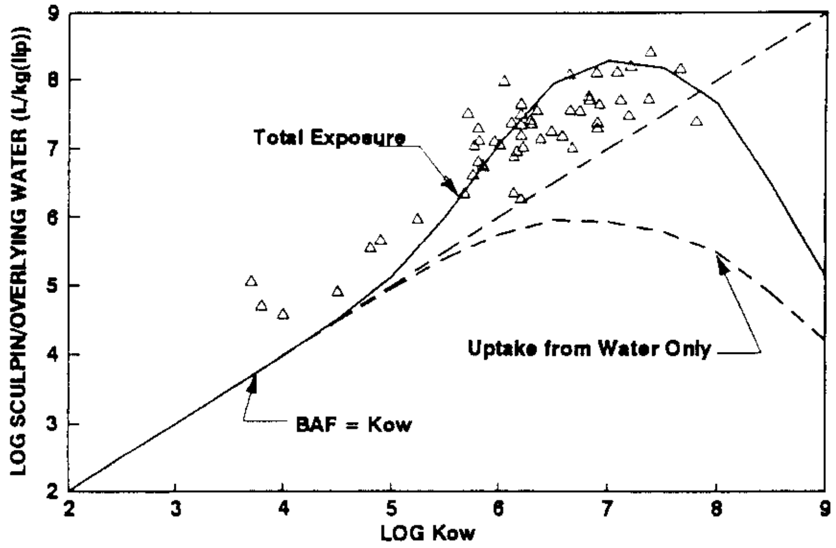


Fig. 7. Calculated factors contributing to amphipod BSF.

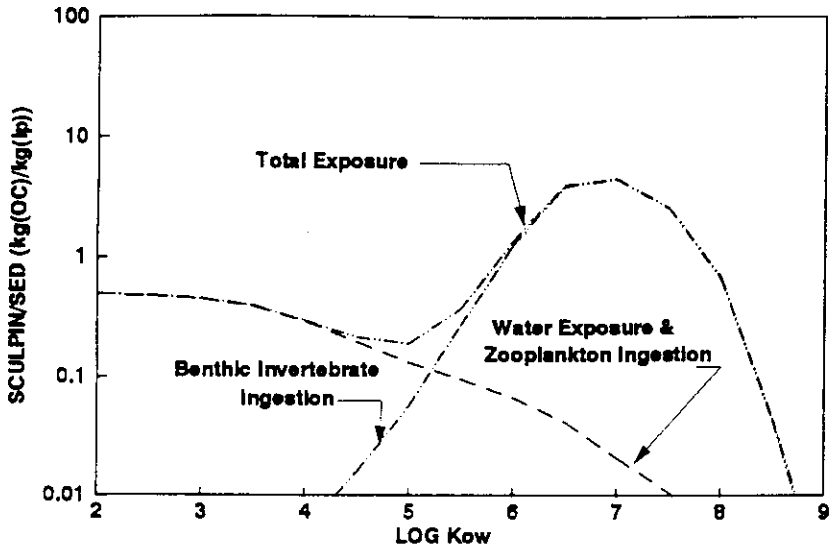


(a) BSF

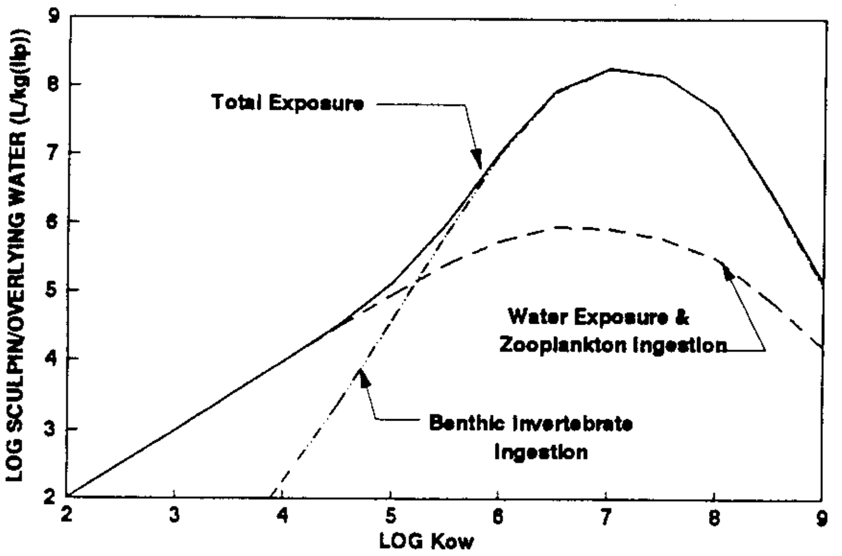


(b) BAF

Fig. 8. Comparison of observed (a) BSF and (b) BAF data of Oliver and Niimi [9] to calibrated sculpin model using parameters of Table 2 and assuming 70% consumption of amphipods.



(a) BSF



(b) BAF

Fig. 9. Calculated contribution from the benthic invertebrate ingestion and water exposure and zooplankton ingestion routes to sculpin (a) BSF and (b) BAF.

Figure 8 shows the computed sculpin BSF and BAF compared to the observed data. The sculpin are considered a forage fish, represented by compartment 3. A similar sensitivity analysis was used for the calibration. For this computation, the amphipod parameters are from Figure 5 and the sculpin are assumed to consume 70% benthic invertebrates and 30% zooplankton. As seen, above a log K_{ow} of about 5, this model indicates that virtually all of the sculpin chemical concentration is due to uptake from the food route.

Figure 9 displays the contribution to the BSF and BAF from the sediment route and indicates in a manner similar to that of the benthic case that almost all of the calculated BSF and BAF for the forage fish is due to the ingestion of benthic invertebrates.

As a final measure of model calibration, Figure 10 shows the ratio of sculpin to amphipod concentration. The data for this ratio do not depend on uncertainties in water column or sediment measurements. The relative importance of the steady-state assumption for π_{ws} is illustrated. By using the "deviation from steady state" representation of π_{ws} in Figure 3 (bottom), the calibration is much improved in the log $K_{ow} < 5$ region. Beyond that

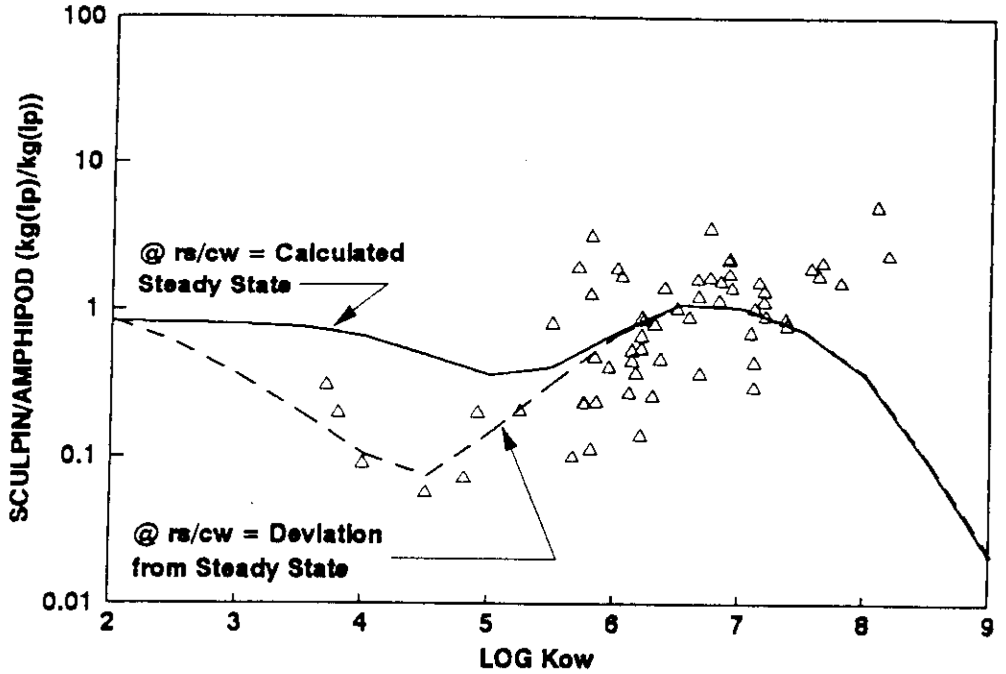


Fig. 10. Comparison of model sculpin-to-amphipod ratio to observed data of Oliver and Niimi [9].

point, the differences are not significant because the steady state is close to the observed π_{ws} data. The data for $K_{ow} > 7.5$ are not captured due to overestimation of the amphipod BSF. The calculated ratio reaches a maximum of about 1.0, indicating no bioaccumulation from the amphipods to the sculpin. This does not imply, however, that the food route is not significant as displayed earlier.

CONCLUSIONS

Normalization of organic chemical concentration to lipid content and sediment chemical concentration to organic carbon content simplifies the calculation of chemical transfer in aquatic food webs with a sediment interaction. The inclusion of a benthic compartment in an equilibrium food-web chemical transfer model, in general, introduces a degree of site specificity and lessens the applicability of a global generic modeling framework. If a forage fish is closely tied to the sediment and benthic invertebrates are exposed only to interstitial water and feed exclusively on sediment organic carbon, then the sediment route dominates. Furthermore, for log K_{ow} greater than about 6, some simple relationships can be obtained between sediment and benthic forage fish concentrations.

From a BAF perspective, the significance of the sediment route is a function of the feeding preference of a forage fish for benthic organisms and the ratio of the sediment–water column partition coefficient to K_{ow}.

Calibration of the model to the site-specific data of the Lake Ontario amphipod indicates that a simple model that considers only two primary exposure routes (i.e., interstitial water and ingested sediment organic carbon) is not a good representation of the observed data. If exposure to overlying water and feeding of overlying plankton are considered, the model more satisfactorily represents the observations. The amphipod BSF and BAF for log K_{ow} greater than about 5 are calculated to be due entirely to ingestion of sediment chemical, with very little due to exposure to dissolved-phase chemical concentration.

For Lake Ontario sculpin, model calibration indicates a combination of feeding on amphipods and plankton. For log $K_{ow} > 5$, BSF and BAF are also calculated to be due almost entirely to the sediment transfer route. Sculpin BAF exceeded K_{ow} by about an order of magnitude for log K_{ow} from about 5.5 to 7.0. The degree of deviation of the sediment–water column partition coefficient from a steady-state condition influenced the model results in the region of log $K_{ow} < 5.0$. For this region, calculated values of sculpin:amphipod ratio are less than those calculated with a theoretical steady-state sediment-water partitioning.

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