5 MODELING THE ACCUMULATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY THE AMPHIPOD *DIPOREIA* (SPP.)

INTRODUCTION

Benthic organisms are exposed to an array of chemical contaminants associated with sediments. One of the important chemical classes of sediment-associated contaminants in the Great Lakes are the polycyclic aromatic hydrocarbons (PAH) (Nriagu and Simmons 1984). Because PAH have low water solubilities and sorb to settling particles, PAH are transported rapidly to the sediments. The settling organic matter and sediment detritus in turn act as food and PAH sources for benthic invertebrates (Landrum et al. 1985, Eadie et al. 1985). High levels of PAH have been found in various benthic organisms of the Great Lakes (Eadie et al. 1985).

Among the important benthic organisms in the Great Lakes ecosystem, the amphipod *Diporeia* (spp.) represents the major benthic invertebrate on a mass basis (Marzolf 1965) and constitutes 65% of the Lake Michigan benthic fauna (Nalepa 1989). (Note: classification of the amphipod *Diporeia* (spp.) is a recent reclassification from *Pontoporeia hoyi* (Bousfield 1989). Additionally, this amphipod readily accumulates nonpolar organic contaminants from both water and sediment with no apparent biotransformation (Landrum 1988, 1989). Because of the importance of this amphipod as a major food source for many fish in the Great Lakes (Mosley and Howmiller 1977), an improved interpretation and understanding of the routes and rates of accumulation for PAH was warranted.)

Mathematical models are often developed to synthesize laboratory and field data for the purpose of understanding observed environmental processes. These models are also useful for identifying those areas that require additional study. The model described in this study examines the movement of nonpolar organic

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contaminants, specifically PAH, into the benthic food chain, specifically the amphipod *Diporeia*. This model is a kinetics-based model that predicts the accumulation of PAH from both sediment and water. The output of the model is compared with measured concentrations of PAH in *Diporeia* and the results of sensitivity and uncertainty analyses of the model are described.

MODEL STRUCTURE

The basic structure of the model involves the calculation of the accumulation and loss of PAH congeners over time using the following rate equation:

$$dC_a / dt = K_w C_w + K_s C_s - K_d C_a \quad (1)$$

where

K_w = Uptake clearance from overlying water (ml overlying water·g^{-1} wet weight organism·h^{-1})
K_s = Uptake clearance from sediment (g dry sediment·g^{-1} wet weight organism·h^{-1})
K_d = Elimination coefficient (h^{-1})
C_a = PAH concentration in the organism (ng contaminant·g^{-1} wet weight)
C_w = PAH concentration in the overlying water (ng contaminant·ml^{-1})
C_s = PAH concentration in the sediment (ng contaminant·g^{-1} dry weight)

Each of the rate coefficients, represented by the K values, are empirical coefficients that represent the combined effects of contaminant characteristics, organism characteristics, and environmental parameters on contaminant uptake and elimination rates. From previous studies (Landrum 1988, 1989), the most important parameters affecting the K terms include contaminant hydrophobicity, organism mass, and environmental temperature. Therefore, the model structure was designed to incorporate the time varying effects of these parameters over the course of a year.

The model selects the initial K values for a compound after the log octanol:water partition coefficient (log K_{ow}) is entered based on regression equations: $K_w = -84.4(\pm30.0) + 53.5(\pm6.3) \log K_{ow}$ ($r^2 = 0.95$, n = 6; Landrum 1988); $\log (1/K_d) = 0.26(\pm0.03) \log K_{ow} + 0.05(\pm0.02)$ mass (mg) $+ 0.99(\pm0.22)$ ($r^2 = 0.55$, n = 73; Landrum 1988) and $K_s = 0.589(\pm0.21) - 0.479(\pm0.039) \log K_{ow}$ ($r^2 = 0.9$, n = 19; Landrum 1989). Initial values for the coefficients are subsequently modified to account for changing temperature and organism mass for K_w as the simulation proceeds. The mass dependence for the coefficients was derived from measures of mass variation of the natural *Diporeia* population that was collected during the same period that the laboratory kinetics studies were performed. The mass of the animals ranged from approximately 3 mg/animal in late January increasing

linearly to approximately 9 mg/animal by October and holding steady through November (Landrum 1988). This mass dependence has only been examined for the coefficients governing uptake from overlying water and elimination. The mass effect becomes statistically insignificant for K_w when the log K_{ow} is less than about four and for K_d when the log K_{ow} is less than about three (Landrum 1988). The change in K_w is evaluated as $\delta K_w = -35.3 + 9.0 \log K_{ow}$ for compounds of log K_{ow} greater than four. Then K_w is corrected by subtracting δK_w * mass (mg) from the initial estimate of K_w. The effect of mass on K_d is part of the initial equation.

The effect of temperature on both the uptake and elimination coefficients are then incorporated using the relationships determined from laboratory studies (Landrum 1988). The temperature profile for each day of the year is generated from an algorithm created for Lake Ontario (McCormick and Scavia 1981). The thermal correction for K_w is constant, 10.9 ml $g^{-1}h^{-1}°C^{-1}$ above or below 4°C, for all compounds with log K_{ow} greater than four (Landrum 1988). For K_d, the effects of temperature varied with season such that the K_d increased by 0.0016 $h^{-1}°C^{-1}$ above 4°C and remained constant below 4°C for Julian days 0 to 150 and 321 to 365 and increased 0.0003 $h^{-1}°C^{-1}$ above 4°C from Julian day 151 to 320 (Landrum, 1988). The thermal regime can vary with depth and provides a daily average temperature but will not provide alterations that might occur with upwelling or downwelling events.

There have not been sufficient studies to determine if K_s exhibits either mass or thermal dependence. The coefficient is assumed to exhibit both but the magnitude is unknown. For this model, we assumed that the initial sediment uptake coefficient, as determined by log K_{ow}, would vary over time in proportion to the changes that occur in K_w due to the effects of mass and temperature. The uptake from sediment was not segmented into uptake from interstitial water and particle ingestion but was instead the overall apparent first-order rate coefficient on a dry sediment basis.

The model generates a rate coefficient for each day of the year and will accommodate any number of measures of overlying water and sediment concentrations. The model uses a step approach to changes in the concentration in the water and sediment concentrations. The initially specified water or sediment concentration remains constant until a new concentration is specified for water or sediment at a specific day of the year. The new value then remains in effect until again changed. Thus, water and sediment concentrations are determined for each day of the year. The concentration in the organism is calculated by adding the net accumulation for a 24-hour period to the concentration in the organism from the previous day (Equation 1). When the model is begun, the concentration in the organism is zero. Because a zero concentration is probably not appropriate, since even neonates will have some contaminant load from their parents, the concentrations used for comparisons with field data are taken from the second simulation year. The initial values of water and sediment concentrations for julian day one were set to those measured on julian day 99 (the first day these

concentrations were measured) except for benzo(a)pyrene (BaP) (Table 1). The BaP water concentration was set to that measured on julian day 109 (Table 1). The water concentration measured on julian day 99 for BaP was thought to be too large based on the concentrations measured for other PAH of similar characteristics.

MATERIALS AND METHODS

Uncertainty and Sensitivity Analyses

In an effort to quantify the model's uncertainty and to establish error bounds around the predicted animal concentration, an uncertainty analysis was used to estimate the overall variance of model output originating from the variance of uncertain model parameters. In order to determine which variables contributed most to the model's uncertainty, we first performed a sensitivity analysis on the eleven principle model parameters (Table 2). We defined the variability for the model parameters in terms of their standard errors from laboratory based regression analyses for all the terms except the initial animal mass and the effect of mass on the uptake clearance coefficient (Table 2) (Landrum 1988, 1989). For those two terms the range was limited to one standard deviation on either side of the mean value based on the mass range observed during the year (Table 2). The uncertainty associated with the measured contaminant concentration in the water and sediment due to natural variability and analytical measurement error were not included in this analysis.

To serve as a means for comparing simulation results, a base simulation was generated by setting all eleven parameters equal to their respective mean values. Then, one by one, model simulations were generated by setting each variable equal to plus or minus one standard error (or standard deviation for the mass influenced terms) of the mean values, while keeping the remaining 10 variables at their mean values (Table 2). All simulations were run for two years using phenanthrene (Phe) ($\log K_{ow} = 4.16$), and BaP ($\log K_{ow} = 6.5$). Finally, the degree of model sensitivity to each of the parameters was estimated as the absolute value of the daily percent deviation (from the base simulation) averaged over the second year of simulation for the predicted animal concentration.

Only those parameters to which the model was most sensitive (> 5% deviation from the base simulation) were used for a limited uncertainty analysis. The analysis was performed by generating a series of unique two-year model runs using all possible combinations (n = 2187) of the selected parameter settings [three settings for each parameter — minimum (mean minus SE or SD), mean and maximum (mean plus SE or SD)]. All other model components, including initial conditions, model coefficients, and hydrological conditions, were identical for each simulation. The time-varying envelope of model behavior, model uncertainty, was determined by calculating the daily mean, standard deviation, an coefficient of variation of the predicted second year animal concentrations that resulted from above simulations.

Table 1. Concentrations of PAH Congeners in Lake Michigan Water ($ng \cdot ml^{-1}$), Sediments ($ng \cdot g^{-1}$), and *Diporeia* ($ng \cdot g^{-1}$)

Julian Day	Phe	Flanth	Pyrene	BaA	BkF	BeP	BaP
Water							
99	0.043	0.0075	0.019	0.0043	0.0237	0.0011	0.020[a]
109	0.104	0.0043	0.017	0.004	0.0032	0.0035	0.001
122	0.151	0.0203	0.018	ND	0.0046	0.0050	0.0035
170	0.177	0.0134	0.025	0.0017	0.0032	ND	0.0168
187	0.250	0.025	0.035	0.0012	0.0035	0.0059	0.0030
211	0.299	0.0262	0.036	0.0733	0.0140	0.0060	0.0216
233	0.240	0.0215	0.026	0.0029	0.0058	0.0053	0.0098
270	0.287	0.0269	0.028	ND	0.0041	0.0192	0.0069
304	0.420	0.0215	0.030	0.0018	0.0129	0.0210	0.0143
324	0.199	0.0220	0.021	ND	0.0211	0.0094	0.0034
344	0.204	0.0281	0.026	ND	0.0108	0.0106	0.0061
Sediment							
99	6	5	5	4	1	4	6
233	58	26	21	9	6	19	12
344	27	51	46	26	17	55	40
Diporeia							
99	64±23[b]	50±44	58±38	48±45	36±25	52±8	49±36
109	74±11	31±7	44±9	15±2	9±2[c]	19±22	4±1[c]
122	98±7	81±53	57±14	31±2	20±6	69±12	219±31
187	723±4[d]	167±18	192±55	95±6	105±64[d]	139[e]	92±71
211	300±95	92±17	39±6	45±7	3±1[c,d]	78±8	17±8
233	640±40[d]	56±10	35±11	31±11	172±96	57±19	94±47
270	49±18	59±9	56±13	29±4	24±1	73±9	41±11
304	43±10	49±7	57±4	30±9	11±1	119±45	73±57
324	47±16	40±6	52±6	28±5	32±10	110±25	44±6
344	52±1	65±4	74±0	53±55	18±9	73±44	28±14
CV							
	1–36	16–88	1–66	17–104	9–70	11–117	8–77

Note: ND = not detected, Phe = phenanthrene, Flanth = Fluoranthene, BaA = Benz(a)anthracene, BkF = Benzo(K)fluoranthene, BeP = Benzo(e)pyrene, BaP = benzo(a)pyrene, CV = range of coefficients of variation (1SD/mean) in units of percent for sediments and organisms.

Table 1. (continued)

[a] This concentration was not used in the model for simulation purposes. The concentration was judged too large for the time of year and out of line with other PAH of similar characteristics.
[b] Mean ± sd, n=3.
[c] Concentrations in question. Data are inconsistent with rest of the data for this compound.
[d] Mean ± range/2, n = 2.
[e] One sample only.

Table 2. Observed Mean and Range of the Uncertain Model Parameters

Parameter	Minimum (–SE or SD)	Mean	Maximum (+SE or SD)	%Deviation from base BaP	%Deviation from base Phe
Uptake rate constant from water, K_w					
K_{ow} slope term[a]	47.2	53.5	59.8	36	21
Mass term[a]	0.5	1.0	1.5	64	5
Temperature term[a]	9.4	10.9	12.4	<5	<5
K_{ow} constant term[a]	54.4	84.4	114.4	26	24
Uptake rate constant from sediment, K_s					
K_{ow} slope term[b]	0.440	0.479	0.518	<5	<5
K_{ow} constant term[b]	0.568	0.589	0.610	<5	<5
Depuration rate constant, K_d					
K_{ow} slope term[a]	0.23	0.26	0.29	41	29
Mass term[a]	0.047	0.049	0.051	<5	<5
Temperature term[a]	0.00014	0.0003	0.00046	12	3
K_{ow} constant term[a]	0.77	0.99	1.21	46	52
Initial animal mass[a]	0.2	3.2	6.2	31	25

[a] From Landrum (1988).
[b] From Landrum (1989).

Analytical Methods

Thirty liter samples of overlying water, collected 1 m above the bottom, and *Diporeia* were collected for PAH analysis approximately monthly at a site nearshore, 29 m deep in Lake Michigan. Collections were not made when prohibited by ice or weather. This nearshore station is frequently influenced by upwelling and downwelling events. Sediment samples (0 to 2 cm) were collected at the same site three times during the year: spring, summer, and fall. Filtered water samples were liquid-liquid extracted while sediments and *Diporeia* were soxhlet extracted. Yields were calculated from the addition of radiolabeled ^{3}H-BaP and ^{14}C-Phe. The PAH concentrations were measured by gas chromatography using photoionization detection for sediment, *Diporeia* and water (Table 1) (Eadie et al. 1988). The water and sediment concentrations were used to parameterize the model and the predicted concentrations in *Diporeia* were compared with the measured values.

Because the measured concentrations were at discrete times of the year and the model provides daily concentrations, the model results for a specific julian day were compared with the field results for that day. A value was calculated that would normalize each day's results, as follows:

Relative Predictability (RP) = model predicted value/field measured value

This relative predictability (RP) can then be compared between various days or averaged and compared between compounds. Values greater than one indicate an over-prediction and values less than one indicate an under-prediction.

RESULTS

The sensitivity studies indicated that the model was very sensitive to changes in the factors that dictate the uptake from water and the elimination of the compound. Changes in the terms for accumulation from the sediment environment seem to be less important. The model was particularly sensitive (percent deviation from base simulation > 5%) when subjected to maximum and minimum values of 7 of the 11 variables tested (Table 2). These included the terms for the slopes and constants of the equations used to select both the initial K_w and K_d values from K_{ow}, the mass dependence term for K_w, the temperature dependence of K_d, and the initial animal mass. The model was not significantly sensitive to the temperature dependence of K_w, the mass dependence of K_d, or to any terms in the equation describing the uptake from sediment. The greatest source of model variability for the BaP simulation was generated by the mass dependence of K_w (percent deviation from base = 63.6%). For the Phe simulation, the greatest source of model variance originated from the constant term in

the depuration rate constant equation (percent deviation from base = 52.4%). The mass-dependence of the K_w term was the only parameter to show a strong compound dependence — the model was much more sensitive to this parameter for BaP (percent deviation from base = 63.6%) than it was for Phe (percent deviation from base = 5.1%).

Model prediction depends on the proper model formalism, appropriate relationships between variables, and on the appropriate parameterization. When there is uncertainty in the relationships between the variables or in the analytical results used to parameterize the model, both may cause failure of the model to predict the observed values. The uncertainty related to the analytical results was not formally introduced into the uncertainty analysis but will contribute significantly to the overall accuracy and uncertainty of the model predictions. The measurement uncertainty for the sediments and the organisms was similar (Table 1) and averaged approximately 50%. Although only single water samples were analyzed for this study, other water samples measured in our laboratory have yielded similar precision to those of the sediments and organisms. Because the water concentration is such a sensitive value, its large uncertainty has a major impact on the ability of the model to predict the observed concentrations in the organisms. In addition, frequent upwelling/downwelling events very likely affect the ambient water concentration significantly (Eadie et al. 1988).

The model uncertainty analysis produced a relatively large envelope around the predicted animal concentration for both the Phe and BaP simulations, represented as the mean of the model output plus or minus one standard deviation (Figure 1). The daily means and standard deviations were calculated from 2187 model runs (= 3^7, seven most sensitive parameters, three settings per parameter). Normalizing the daily standard deviations to the daily means produced time-varying coefficients of variation which ranged between 41% and 110% (annual mean = 62%) for the Phe simulation and between 66% and 108% (annual mean = 86%) for the BaP simulation. The coefficient of variation was negatively correlated with the mean predicted animal concentration ($r = -0.711$ for Phe, $r = -0.789$ for BaP), implying a decrease in relative model uncertainty with increasing animal body burdens.

Initial comparisons of the model results to the field measured values suggests that the model was less able to predict organism contaminant concentrations for the contaminants with smaller log K_{ow} values. For all log K_{ow} values, the RP was greater than one and in several cases the values were greater than one hundred (Figure 2). The excessive predictability, values greater than one hundred, seemed to be limited to six values: four for Phe and two for benzo(k)fluoranthene (BkF). If these values are considered outliers, most of the RP values fall below 30 (Figure 3). However, the general trend of larger RP values with smaller log K_{ow} values remains.

An improved fit of the model predictions to the field observations results when the overlying water concentration is reduced by a factor of ten. Reduction of the overlying water concentration was attempted as the first adjustment of

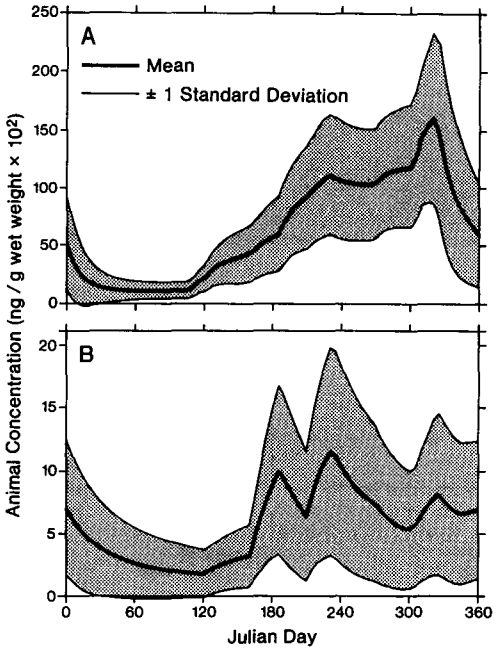

Figure 1. The envelope of the uncertainty for the predictions of Phe (a) and BaP (b) when the overlying water concentration was the measured value.

model parameters because of the large uncertainty in the analytical measurement for water and the sensitivity of the model to this parameter. This manipulation results in RP values of less than eight with most less than four (Figure 4). Again this excludes the original outliers in the data set. The model was better able to predict the *Diporeia* concentrations for the larger log K_{ow} compounds. For the case of BaP, the RP averages 1.4 ± 1.1 (mean ± sd, n = 9) and for benzo(e)pyrene (BeP) the RP averages 0.75 ± 0.45 (mean ± sd, n = 10). However, the model continued to over-predict the *Diporeia* concentrations for the compounds with smaller log K_{ow} values.

Keeping the overlying water concentration reduced by a factor of ten and examining each of the predicted and measured values permits examination of temporal patterns. Concentrations of compounds with large log K_{ow} values such as BaP and BeP are relatively well predicted, within about a factor of two, except for some values in the spring where the measured value is much larger than the predicted value (Figure 5a and b). Generally the predicted concentrations produce the same seasonal pattern as the measured concentrations. The other compound with a relatively large log K_{ow}, BkF, is not predicted well and the seasonal pattern of the predicted to the measured values seems random (Figure 5c). Concentrations of benz(a)anthracene (BaA), a compound of more interme-

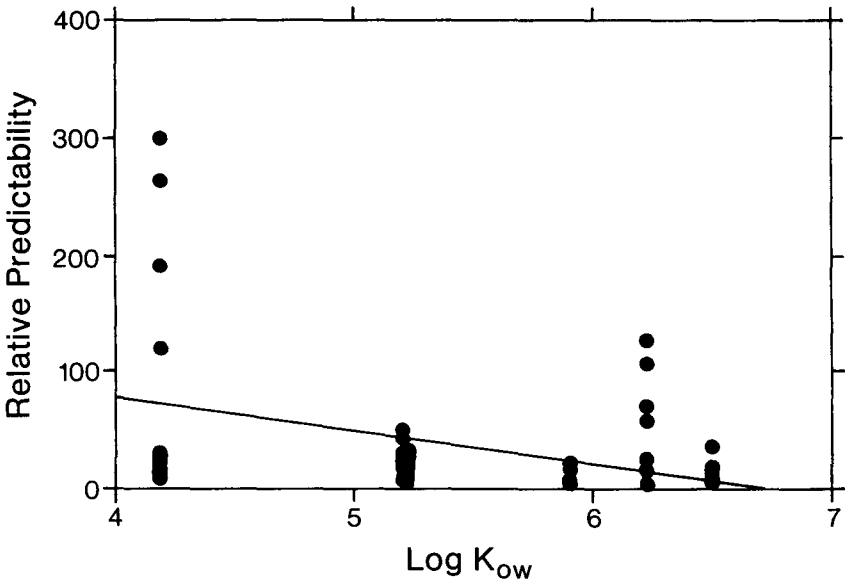

Figure 2. Relationship between the relative predictability and log K_{ow} for all the predictions using the measured overlying water concentrations.

diate log K_{ow}, are also predicted relatively well except for one value (Figure 5d). This high predicted value for BaA is created by a single water concentration that is more than ten times larger than all the other measured concentrations. In summary, for compounds with log K_{ow} values near six, model predictions are most reasonable when the water concentration is reduced by a factor of ten. Generally, the difference between the measured and predicted values was less than a factor of two.

For compounds with log K_{ow} values about five or less, even with the water concentration reduced by a factor of ten, the predictive power of the model is limited. In general, the concentrations in the organisms are over estimated by the model simulation (Figure 5 e,f,g). For these low log K_{ow} compounds, the overprediction is more dramatic for the later summer and fall samples compared to the winter through early summer. This generally reflects a large increase in the measured sediment concentrations in midsummer which begins to contribute substantially to the increase in the predicted organism concentrations. The measured sediment concentrations do not increase as markedly for the compounds with the larger log K_{ow} values (Table 1).

Closer examination of the flux of material into the organism for BaP, a large K_{ow} compound, shows that the predicted concentration in the organism is dominated by the flux from the overlying water year round (Figure 6a). The flux from the sediment has little impact on the predicted values even when the

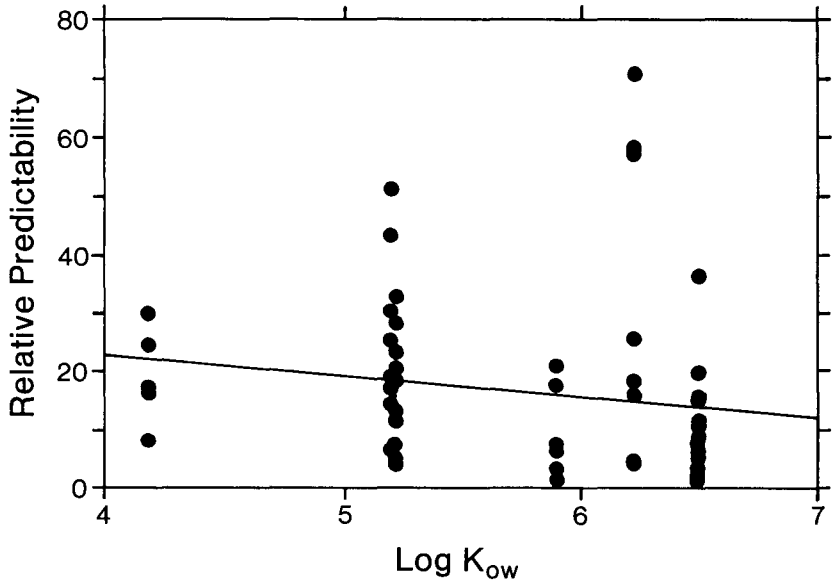

Figure 3. Relationship between the relative predictability and log K_{ow} after removing six outliers and using the measured overlying water concentrations. Relative predictability = 37.1 (± 14.7) – 3.5 (± 2.55) · log K_{ow} (n = 62, r^2 = 0.31, p = 0.17).

concentration in the overlying water is reduced by a factor of ten (Figure 6b). For Phe, a low K_{ow} compound, the flux from the overlying water dominates the accumulation as observed for BaP (Figure 6c) but when the water concentration is reduced by a factor of ten, the greater midsummer sediment concentrations contribute significantly to the predicted concentrations (Figure 6d). The pattern of accumulation for low K_{ow} compounds observed in the organisms is not reproduced in the model due to both higher measured sediment and overlying water concentrations in midsummer.

DISCUSSION

For a model to accurately predict the *Diporeia* concentrations, the proper model formalism, appropriate relationships between variables, and the appropriate parameterization are required. Why, then, does the model generally over-predict the concentrations observed in the field? First, the model may not have the proper formalism. The model employed for this study describes exposure to two sources, overlying water and sediment, with continuous exposure to both. These exposures may not be continuous. For overlying water, the exposures may well be discontinuous since *Diporeia* spend most of their time buried in the sediments

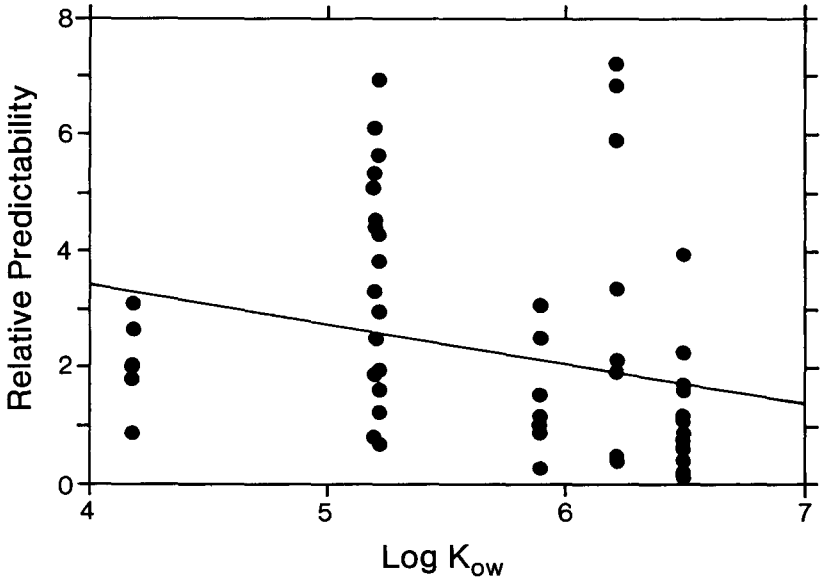

Figure 4. Relationship between the relative predictability and log K_{ow} after the overlying water concentration was reduced by a factor of ten. A relative predictability of one means the predicted value and the measured value are equal. Relative predictability = 5.5 (± 2.1) – 0.55 (± 0.37) · log K_{ow} (n = 62, r^2 = 0.35, p = 0.14).

with only short excursions up into the overlying water. It is estimated that these excursions account for less than ten percent of the organisms' life span (Quigly, M.A., 1990, personal communication, Great Lakes Environmental Research Laboratory, Ann Arbor, MI). Because the flux from the overlying water into the organisms results from both the concentration and the exposure time, with the current model formalism, a reduction of the concentration would be functionally equivalent to a reduced exposure duration. Reducing the simulated flux from the overlying water by decreasing the water concentration by a factor of ten seems appropriate because of the improved predictions, particularly for the compounds with larger log K_{ow} values.

The other exposure that is modeled as continuous is accumulation from sediment. This exposure does not distinguish between accumulation due to ingestion or from the interstitial water, although ingestion of sediment detrital material is thought to strongly contribute to the flux from sediment, particularly for compounds with large K_{ow} values (Landrum and Robbin 1990). Some limnological studies show that this organism seems to be an intermittent feeder (Quigley 1988) and feeds heavily on the pulse of diatom detritus in the spring,

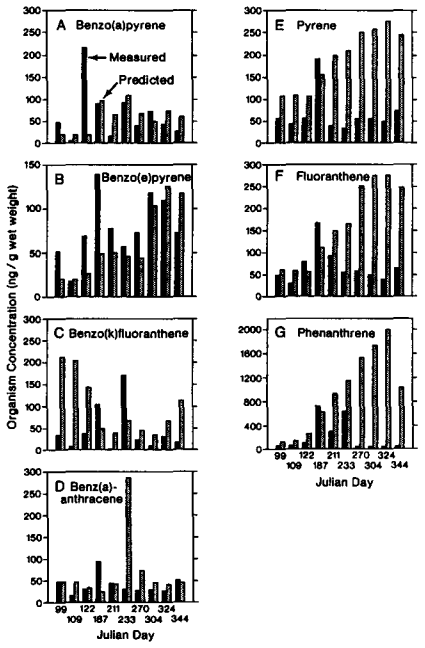

Figure 5. The comparison between the model predicted and the measured concentration of seven PAH congeners (a to g) over the course of one season.

particularly at the nearshore station that was modeled here (Gardner et al. 1985). Further, the PAH concentrations of this detrital matter are approximately a factor of five to ten greater than for the fine sediments (<53μm) (Eadie et al. 1988). Thus, freshly ingested particles should present *Diporeia* with a large pulse of contaminant in the spring and early summer when they are apparently feeding on the "raining" detrital material. Our knowledge of the model input parameters does not permit us to account for the discontinuous feeding or the potential pulse from the diatom detrital pulse. However, for compounds with large K_{ow} values, where accumulation from ingested particles is likely most important, the model yields the best predictions. Thus, not accounting for the discontinuous feeding and feeding on the spring diatoms may not be important to predicting the daily average flux of contaminant into *Diporeia*.

Finally, within the limits of the existing data, it was not possible to establish a more mechanistically based model such as an energetics model. Construction of this type of model is limited because of limited physiology, growth, and behavior data for *Diporeia* as well as constructs between these parameters and contaminant accumulation. For instance, there are only two measures of assimilation efficiency for organic compounds ingested with sediment detritus for

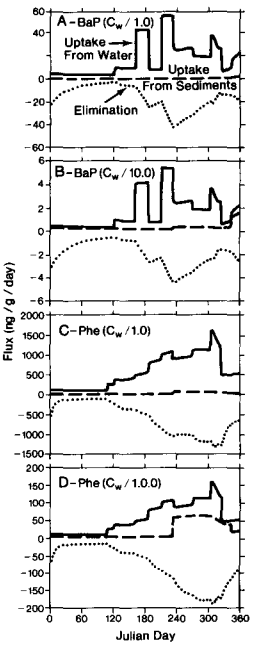

Figure 6. The fluxes for the accumulation and loss of BaP (a,b) and Phe (c,d) over the course of one season when the overlying water concentration was the measured values (a,c) and was reduced by a factor of ten (b,d).

invertebrates (Lee et al. 1990, Klump et al. 1987), and these are for chlorinated hydrocarbons and not PAH congeners. Thus, as with any modeling effort the data limitations sometimes preclude development of more mechanistic models. While relatively good prediction can be obtained for compounds with larger log K_{ow} values, it is clear that improvements in predictability will require refinements in model formalism.

The second potential reason that the model over-predicts the organism concentrations is that the parameterization of the variables may be in error. For instance, the actual overlying water concentrations may be lower than measured values. There was considerable difficulty measuring the low ng l^{-1} concentrations of the individual PAH congeners and in many cases the values were near the detection limit. The difficulty is compounded by inconsistent blanks and potential chromatographic interferences. In a workshop conducted to balance BaP mass in Lake Michigan, the water concentration was calculated to be approximately 0.07 ng l^{-1} (Strahan and Eisenreich 1988). Values of PAH measured in Lake Superior were in the range of 0.02 to 3.49 ng l^{-1} with that for BaP at 0.4 ng l^{-1} (Baker and Eisenreich 1990). These estimates are in the range

of a factor of ten less than the values we measured (Table 1). Thus, the difficulties of making measurements of these extremely low concentrations may have resulted in over estimates of the actual water concentrations.

Further, the method of measurement, liquid-liquid extraction and gas chromatography would measure material associated with colloids or macromolecules in addition to "truly dissolved" compound. Compounds associated with these organic materials are not readily bioavailable (Landrum et al. 1987). Therefore, the measured concentrations are likely larger than the bioavailable concentrations. Finally, the temporal variability observed in the water concentrations is likely caused by frequent upwelling and downwelling that pulse local sediment resuspension. The frequency and magnitude of the true temporal variability may not be completely reflected in the data. Upwelling and downwelling events in nearshore areas occur on a more frequent basis than the sampling schedule. As a result of the wide temporal spread in field sampling, only a partial indication of the variability can be measured.

Choosing to modify the overlying water concentration, before other parameters, to obtain better model predictions is justified from the sensitivity analyses, the uncertainty about the organism's behavior, and the analytical variability. Regardless of the mechanism involved, inappropriate model formalism with regard to organism behavior or errors in analytical measures of PAH concentrations in overlying water, the organism exposure to overlying water would be one tenth that used in the initial model simulation. Reducing the exposure to PAH in the overlying water allowed the model to provide closer predictions, within a factor of about two, of PAH concentrations in *Diporeia* for compounds with a log K_{ow} approximately six. The exception in this study for compounds with relatively large log K_{ow} values was BkF and analytical interferences are suspected as the reason for the difference between model results and measurements.

Differences between the model simulation results and field results for compounds with log K_{ow} values less than six were reduced by adjusting the water concentrations. Nevertheless, there remains a trend in increasing difference between model and field measured concentrations for compounds with smaller log K_{ow} values. Thus, other explanations than reduced exposure to overlying water are required to explain why the simulations for these compounds have reduced comparability with field data. Sediment-associated PAH, particularly those with smaller log K_{ow} values, seem to become less bioavailable with increasing contact time between sediment particles and the contaminant (Landrum 1989). The process that apparently accounts for the reduced bioavailability, i.e., the movement of the compound into the pores of the particles, is likely the same process that reduces chemical extractability (Karickhoff 1980, Karickhoff and Morris 1985, DiToro et al. 1982). However, this bioavailability reduction occurs more rapidly than reduction in chemically measured concentrations (Landrum 1989). If this process occurs in the field, then the chemically measured concentrations in sediment may not reflect the biologically available contaminant. This

would lead to an over estimation of the rate of accumulation from sediments for these low log K_{ow} compounds, since the mathematical formalism expects that all the compound in the sediment is bioavailable. Compounds that have larger log K_{ow} values have not shown this reduced bioavailability (Landrum 1989). Perhaps this occurs because the initial sorption is so strong that the process of migrating into particle interstices is much slower and/or the larger molecular size of the larger log K_{ow} compounds reduces their ability to migrate into pores, thus leaving the compound in a more bioavailable form. In addition to the above potential process, the rate coefficients for accumulation, K_w and K_s, behave differently for BaP and Phe as representatives of large and small log K_{ow} compounds. In the model, these rate coefficients for BaP decline in the summer by about a factor of 1.6 compared to winter values. However, the uptake rate coefficients for Phe increase during the winter to summer transition by about the same factor. These changes reflect the differences in the behavior of the uptake rate coefficients from water, K_w, for the two compounds. This difference is driven primarily by the mass dependence of K_w, which is an important variable modifying the K_w for BaP but is insignificant for K_w for Phe. Since K_s is changed in proportion to K_w, the seasonal difference in the uptake coefficients will elevate the importance of the sediment component in the accumulation of contaminant in the summer and fall, when the over-predictions seem to occur for the smaller log K_{ow} compounds. The difference is exacerbated by the increased measured values of the sediment concentrations. The combination of factors contribute to the overestimation for compounds with smaller log K_{ow} values.

The model suggests that the bulk of the *Diporeia* contaminant accumulation comes from overlying water since the larger uptake fluxes were calculated for the overlying water source. The annual estimate for the fraction of contaminant obtained from overlying water is approximately 75%, with the remaining 25% attributable to sediment uptake for both Phe and BaP when the water concentrations are held at 10% of their measured value. This proportion occurs because of the very large coefficients for the accumulation from water compared to those for accumulation from sediment (Landrum 1988, 1989). The model estimates that the relative contributions from overlying water and sediment are similar to those estimated from previous field work for Phe (Eadie et al. 1985). However, the same field study estimated that BaP would be accumulated primarily from a sediment source; the current model suggests otherwise.

The uncertainty of the model predictions is large, essentially a factor of two, from the variability of the model coefficients alone. The uncertainty contributed by the analytical variation in the parameter estimates will result in even larger uncertainty, particularly with regard to the overlying water contribution. Additional efforts will be best spent refining the analytical uncertainty in the water concentration before attempting to address the uncertainty in the model parameters.

In summary, the model markedly over-estimated the concentrations of PAH in *Diporeia* when parameterized with analytical determinations of water and

sediment concentrations. The model predicted the *Diporeia* concentrations more accurately when the water concentrations were reduced by a factor of ten. Even after reducing the water concentration, the accumulation of compounds with a log K_{ow} of approximately five or less were still over estimated by up to a factor of eight. However, the compounds with a log K_{ow} of near six were generally well predicted except for BkF. After accounting for all the factors that may induce error in the predicted values, the measure of the overlying water concentrations seems the most likely parameter that accounts for most of the over-estimation.

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6 MODELING THE ACCUMULATION AND TOXICITY OF ORGANIC CHEMICALS IN AQUATIC FOOD CHAINS

INTRODUCTION

For the management of contaminants in rivers and lakes, it is important to be able to predict the impacts of a discharge of a single and/or multiple chemicals in terms of chemical concentrations and toxic effects in aquatic biota. Building such a predictive capability requires knowledge of the transport of the chemical from its origin into the organism and of the interaction of the chemical with crucial target sites in the organism. This knowledge can then be captured in computer models, which when peer reviewed, represents the best available knowledge for practical use in water quality management. Further research will improve these models and provide a better predictive ability and management.

Several chapters in this volume discuss the factors that control the water and sediment concentrations in aquatic systems and formulate models that can be used for predicting water and sediment concentrations from chemical discharges. This chapter addresses the uptake and bioaccumulation of organic chemicals from the water and sediments into single organisms and in entire food chains. It summarizes the current state of knowledge regarding the mechanism of chemical uptake and bioaccumulation in various aquatic organisms and it presents a model to predict the accumulation of organic substances in aquatic food chains. It is further shown how this model can be used to assess toxic effects in fish and other aquatic organisms.

We will demonstrate the ability of this "food chain" model to predict chemical concentrations in aquatic food chains by applying the model to experimental data for Lake Ontario. Since the model only requires a small set of basic, and readily accessible data to characterize the food chain, the model is believed to be a practical tool for contaminant management on an "ecosystem" level.

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BIOAVAILABILITY

One of the most important factors controlling the uptake and bioaccumulation of organic chemicals in aquatic organisms, is the concentration of the chemical in the water that can be absorbed by the organism from the water (e.g., via the gills in fish). In particular for very hydrophobic chemicals, the concentration of absorbable or bioavailable chemical is often only a fraction of the total chemical concentration in the water. This fraction is usually referred to as the Bioavailable Solute Fraction (BSF), or simply the bioavailability (Landrum et al. 1985, Black and McCarthy 1988, Gobas et al. 1989a).

The bioavailability of organic chemicals in natural waters is largely determined by the interaction of the chemical with organic carbon-containing materials, which occur both in particulate and in dissolved form. There remains controversy about the state of the chemical when sorbed to the organic matter. The most generally held current belief is that the chemical is dissolved in a solid solution form in, or on, a sponge-like matrix of organic matter, which is too large to permeate through biological membranes (e.g., the gill membrane). Sorption is generally viewed as an equilibrium partitioning of the chemical between the water and the organic matter (OM) in the water column (Karickhoff 1984)

$$\text{Dissolved Chemical} + \text{OM} \Longleftrightarrow \text{Chemical} - \text{OM} \tag{1}$$

which can be expressed by a partition coefficient K_{oc} (l/kg):

$$K_{oc} = C_{WB} / \left(C_{WD} \cdot [OM]\right) \tag{2}$$

where C_{WB} (μg/l) is the concentration of "bound" or "sorbed" chemical, i.e., ($C_{WT} - C_{WD}$), C_{WD} is the concentration of dissolved chemical (μg/l) and [OM] is the concentration of organic matter in the water (kg/l). Based on the hypothesis that only chemical in true solution is bioavailable, the bioavailability can be defined as the ratio of the truly dissolved chemical concentration in the water C_{WD} (μg/l) and the total chemical concentration in the water C_{WT}(μg/l), i.e.,

$$BSF = C_{WD} / C_{WT} \tag{3}$$

Since, it has been suggested that within experimental error, K_{oc} equals K_{ow}/d_{oc} (DiToro 1985), the following expression can be derived by substituting Equation 2 in Equation 3 to estimate the bioavailability of organic chemicals in natural waters.

$$BSF = 1 / \left(1 + K_{ow} \cdot [OM] / d_{oc}\right) \tag{4}$$

Chemical Dynamics in Fresh Water Ecosystems

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