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Bioaccumulation of PCB Congeners by *Diporeia* spp.: Kinetics and Factors Affecting Bioavailability

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ABSTRACT. *The toxicokinetics of four polychlorinated biphenyl (PCB) congeners were determined for the amphipod* Diporeia *spp. exposed to selected PCB congeners through both water and sediment to determine the effect of temperature and organism size (mass). For compounds with log K_{ow} 6 or greater, the water-only uptake coefficient (k_u) was inversely proportional to the size of the organism at all temperatures. For monochlorobiphenyl, k_u was directly proportional to organism mass only at 16°C. Increasing temperature resulted in increasing uptake rate coefficients for all compounds except hexachlorobiphenyl (HCBP) where k_u did not appear to depend on temperature. The hydrophobicity of the contaminants did not contribute significantly to changes in uptake rate from water. The elimination rate constant (k_e) was inversely proportional to organism size but was not significantly affected by temperature. The elimination rate constant declined exponentially with increasing log K_{ow}. As log K_{ow} increased, the effect of organism mass on k_e was greatly reduced. The uptake from sediment was affected by temperature and the congener log K_{ow}. At lower temperatures, the uptake coefficient from sediment (k_s) declined with increasing log K_{ow}, while at higher temperatures, it exhibited a slight upward trend. Smaller animals had much higher uptake rates from sediment than large or medium size animals. Small animals exhibited very high biota-sediment accumulation factors (5.4 to 20.8) over 4 to 16°C for HCBP (BSAF, concentration in the organism normalized to the lipid content divided by the concentration in the sediment normalized to the organic carbon content). The relationship between BSAF and log K_{ow} was exponential for both laboratory and field data.*

INDEX WORDS: Diporeia *spp., PCB, toxicokinetics, organism size, temperature, BSAF.*

INTRODUCTION

Accumulation of contaminants by benthic organisms may occur via any of several routes: ingestion of sediment particles, respiration of interstitial water, respiration of overlying water, ingestion of freshly deposited food particles, and/or across the integument through contact with any of the above source compartments. Resolving the factors and routes of accumulation are necessary to develop accurate predictions of bioaccumulation. Recent attempts to include the benthic food web in predictive bioaccumulation models indicate that benthos contribute significantly to the food web transfer of organic contaminants in the Lake Ontario system. Thus, improved data on the accumulation of contaminants by benthos, particularly in this system, are necessary to accurately quantify the influence of sediment-associated contaminants (Thomann *et al.* 1992, Morrison *et al.* 1996).

Diporeia spp. constitutes the major benthic invertebrate in the Great Lakes based on its biomass; although its status may be changing due to recent declines in population (Dermott and Kerec 1997, Nalepa *et al.* 1998). The importance of *Diporeia* spp. and its ecotoxicology were recently reviewed (Landrum and Nalepa 1998). From this review, several factors governing the importance of *Diporeia*

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are clear: 1. It is a major prey item for most fish. 2. It can accumulate high concentrations of organic contaminants because of its high lipid content. 3. It has no apparent ability to offset the high accumulation by biotransformation. 4. It is exposed to sediment contaminants by burrowing into and ingesting sediments. These features make *Diporeia* an ideal organism for transferring contaminants from sediment to the food web.

Seasonal changes in the concentration of polycyclic aromatic hydrocarbons, such as benzo(a)pyrene (BaP), in *Diporeia* have been observed (Landrum *et al*. 1992a). While such changes are apparent in both the field data and through modeling exercises, the ability to predict the field data remains poor (Landrum *et al*. 1992a). This likely results from two factors: 1. The contribution from various potential sources is not well defined, and/or 2. Physiological changes in the organism were not well incorporated into the models. This work focuses on the influence of factors such as temperature and organism physiology as important features driving the bioaccumulation of contaminants. The objectives were to examine the impact of temperature and organism size on the toxicokinetics of selected PCB congeners from water and sediment.

MATERIALS AND METHODS

Chemicals

^{14}C-4-chlorobiphenyl (MCBP, 17 µCi/µmol; log K_{ow} 4.69 Hawker and Connell 1988), ^{14}C-4,4-dichlorobiphenyl (DCBP, 13.8 µCi/µmol; log K_{ow} 5.3 Hawker and Connell 1988), ^{14}C-3,4,3′,4′-tetrachlorobiphenyl (TCBP, 37.1 µCi/µmol; log K_{ow} 6.36 Hawker and Connell 1988), and ^{14}C-2,4,5,2′,4′,5′-hexachlorobiphenyl (HCBP, 12.6 µCi/µmol; log K_{ow} 6.92 Hawker and Connell 1988) were purchased from Sigma Chemical Company, St. Louis, MO. All compounds were dissolved in acetone carrier. The radiopurity was determined via a combination of thin-layer chromatography on silica gel plates using hexane:benzene (8:2) and liquid scintillation counting (LSC). The radiopurity was found to be > 98% for all compounds.

Organisms

The *Diporeia* spp. were collected from Lake Michigan off Muskegon, Michigan (43.02° N, 86.29° W) in the spring, summer, and fall of 1995 and 1996. Animals were collected by Ponar grab from 29 m depth and were removed from the sediment using a 1 mm screen. *Diporeia* were held in lake water and transported on ice to the Great Lakes Environmental Research Laboratory, Ann Arbor, MI. *Diporeia* were held in the dark at 4°C in shallow aquaria containing 3 to 4 cm of their native sediment overlaid with 7 to 10 cm of unfiltered lake water. Fifty percent of the overlying water was exchanged each week, and animals were held for less than 1 month prior to experimental use. Juvenile animals were sorted into three size classes (small, medium, and large) by visually estimating their weight as being < 3 mg, 3 to 6 mg, or > 6 mg wet weight respectively and placed into exposure containers. However, measured weights were used to place organisms into the appropriate size classes for toxicokinetic calculations. Gravid females were excluded from the experiments. Sorted animals were placed in 5-gallon aquaria with a small amount of Lake Michigan sediment and acclimated to experimental temperatures by increasing the temperature by 2°C per day. Organisms were held at the experimental temperature for 48 h prior to experimental use. At the beginning of each experiment, 10 animals from each size class were removed and placed into tared 6 × 50 mm culture tubes (Kimble Glass Inc., Vineland, NJ, USA) for later analyses of lipid content. Lipids were measured using a micro gravimetric procedure with a chloroform/methanol extraction (Gardner *et al.* 1985).

Animals used to determine biota-sediment accumulation factor (BSAF) values for *Diporeia* spp. from the field were collected in July 1994 by Ponar grab from a 45-m-deep station off Grand Haven, MI (43.01° N, 86.32° W). Sediments were mixed with lake water, and the animals were removed using a 500 mm screen. Animals were screened from the sediment and sorted visually to have a length of greater than 4 mm. The *Diporeia* spp. were then divided into groups of approximately 200 animals, wrapped in ashed aluminum foil, and kept frozen at –20°C in the dark until analysis. In a separate study, the wet weight of the organisms collected in fall 1999, sorted in the same manner, were found to be > 3 mg wet weight with a mean weight of 7.7 ± 0.5 mg wet weight (Sander Robinson, Great Lakes Environmental Research Laboratory, Ann Arbor, MI, personal communication).

Sediment

Sediment used in uptake and elimination studies was collected from Lake Michigan by Ponar grab

at a 45-m-deep station off Grand Haven, MI (43.03°N, 86.37°W), sieved (1 mm Nytex, Tetco, Briarcliff Manor, NY, USA), and stored at 4°C until use. Sediment used to determine the BSAF values of animals from the field was collected from the same site as the organisms (43.01° N, 86.32° W) using a gravity corer. Composites of the surficial (0 to 1 cm) sediments of three core samples were collected and placed in solvent-rinsed glass jars with foil-lined caps. Samples were kept frozen at –20°C in the dark until analysis. Triplicate sub-samples of approximately 3 to 4 g of each sediment were dried at 65°C in order to determine the wet-to-dry weight ratios. This dry sediment was later treated with HCl to remove carbonates, and organic carbon content was measured using a model 2400 CHN Elemental Analyzer (Perkin Elmer Corp., Norwalk, CT, USA).

Experimental

Common Procedures

Water-only uptake, elimination, and sediment uptake studies were conducted with each of the three size classes of *Diporeia* spp. using ^{14}C-labeled MCBP, DCBP, TCBP, and HCBP at temperatures of 4, 8, 12, and 16°C. Huron River water was used for these experiments since its hardness, alkalinity, and pH are very similar to Lake Michigan water (Kane Driscoll *et al*. 1997). All water was filtered through 0.45 mm glass microfibre filters (Whatman Inc., Clifton, NJ, USA). Animals sampled throughout the study were removed from the sediment or water by sieving (500 µm), blotted dry, weighed using a CAHN Model 4700 electrobalance (Ventron Corp. Cerritos, CA, USA), and placed into 12 mL xylene-based scintillation cocktail (3a70b, Research Products International, Mt. Prospect, IL, USA). Triplicate sub samples (100 mg) of sediment were weighed using a Mettler AT250 (Mettler-Toledo, Inc., Highstown, NJ, USA), placed into 12 mL scintillation cocktail, and sonicated for 1 min (375W at 20% power) with a Tekmar (Cincinnati, OH, USA) high-intensity probe-sonicator. The xylene-based cocktail acts as a suitable solvent to extract the PCBs. Both animal and sediment contaminant concentrations were determined by liquid scintillation counting (LSC) on a Packard 2500 TR (Packard Instrument Co., Meriden, CT, USA) using the external standards method for quench correction after subtracting background.

Water-only Uptake

Water for 24-h, static, exposures was dosed with individual compounds using acetone as a carrier (less than 0.5 mL/L). The water concentrations for the aqueous exposures were all in the ppb range: MCBP 1.1 to 1.4 µg/L, DCBP 1.7 to 3.2 µg/L, TCBP 0.8 to 1.4 µg/L, and HCBP 2.9 to 3.6 µg/L. Exposures were carried out in 60 ml BOD bottles (Landrum and Stubblefield 1991). Thirty-nine BOD bottles were set up for each of the four compounds tested; 13 replicate bottles were used for each size class of animal. Bottles were filled to the top with the dosed water and allowed to equilibrate overnight at either 4, 8, 12, or 16°C. Before adding *Diporeia* (two organisms per bottle) and after they were removed, water samples (2 mL) were taken for total contaminant concentration. An additional water sample (2 mL) was passed through C-18 Sep Pak columns (Waters Co. Milford, MA, USA) to determine the proportions of the contaminant that were freely dissolved and bound to dissolved organic-carbon (Landrum and Stubblefield 1991). After 24 h, animals were removed, weighed, and accumulated contaminant in the tissue was determined by LSC.

The accumulation data were fit to a mass balance model (Landrum 1983). Because the data were collected over a short time frame (24 h), elimination is assumed to be unimportant during the uptake exposure, and the system dependent uptake rate constant is calculated as follows (Landrum 1983):

$$k_1 = -\ln(1 - Q_a/A) / t \quad (1)$$

Where k_1 is the conditional uptake rate constant (1/h), Q_a is the total quantity of compound in the organism (ng), A is the total quantity of compound in the system (ng), and t is time (h).

The mass balance uptake constant was converted to an uptake clearance (Landrum 1983). The uptake clearance is system independent and is on a concentration basis.

$$k_u = k_1 \text{ (Volume of Water / Mass of organism)} \quad (2)$$

With the volume in milliliters and the mass in grams, the uptake clearance has units of mL/g/h and describes the volume of source compartment scavenged of contaminant per mass of organism per unit of time.

Because the concentration of the radiolabeled compound in an individual organism could have

been difficult to measure, the average mass of the two organisms in the BOD bottle was used to examine the relationship between k_u and mass. Organisms in the middle and large size classes were weighed separately to ensure that the individual weights did not fall below or above the size class by more than 1 mg.

Elimination

Animals for elimination studies were exposed for 24 h at the same temperature as that used for elimination measurements (4,8,12, and 16°C). The water dosed with either MCBP, DCBP, TCBP, or HCBP via acetone carrier at the same concentrations as used for the uptake kinetics. After exposure, 10 animals from each size class were placed into six 400 mL beakers containing 100 g of uncontaminated wet Lake Michigan sediment and 200 mL of filtered Huron River water. Ten animals of each size class were weighed and analyzed by LSC immediately after dosing to determine the initial contaminant concentration. Animals from one beaker of each size class were sampled after approximately 1, 2, 5, 8, and 16 d (exact times were used for kinetic analysis). In five experiments, an additional time point was added at 20 to 40 d. After the last time point, 10 animals of each size class were sampled for lipid concentration.

As the data were analyzed, animals were placed into the size class indicated by their measured wet weight. Elimination rate constants (k_e) were calculated using a first order elimination model:

$$Ca = Ca^{(t=0)}\, e^{-k_e t} \qquad (3)$$

where C_a is the concentration in the animal (dpm/g), $C_a^{(t=0)}$ is the time zero concentration in the animal, k_e is the conditional depuration rate constant (1/h), and t is time (h). C_a may be converted to ng/g using the appropriate specific activities and molecular weights for the compounds under consideration. Estimates of k_e were calculated by linear regressions of ln C_a verses t. All plots of C_a versus t at 4°C and those for MCBP and DCBP at 8°C revealed a rapid drop in contaminant concentration between time zero and the first sampling point possibly due to surface desorption. It is also possible that this rapid concentration decline was caused by the dilution of the compound as animals resumed feeding and gained weight due to ingested sediment in the gut. Therefore, time zero data were excluded from the regression for these studies. Differences in the elimination rate constant, k_e, between various temperatures and size classes (Landrum *et al*. 1998) were examined using the Student's t test in a pairwise comparison.

Uptake from Sediment

Sediment uptake studies were performed in 1995 and 1996. The sediments were dosed separately for each set of exposures using the EPA-recommended rolling jar method (Kane Driscoll *et al*. 1997, Ditsworth and Schults 1990). The sediment was incubated for 60 d at 4°C so the contaminant would come into near equilibrium between the sediment and interstitial water. The sediment concentrations were in the ppb range for all compounds: MCBP 23.9 to 57.6 µg/kg except for the 12°C study which was at 276 µg/kg, DCBP 40.5 to 87.2 µg/kg, TCBP 20.4 to 36.5 µg/kg, and HCBP 82.8 to 153.5 µg/kg. For each compound at each temperature, 19 beakers (400 mL) containing 50 g wet sediment and 300 mL of water were set up for each size class of animal. Beakers were placed in incubators 1 d prior to the addition of animals. Five animals were placed in each beaker. Approximately 100 mL of overlying water was exchanged three times per week to maintain water quality. Oxygen and pH were monitored with an Accumet 1000 hand held pH meter (Fisher Scientific, Pittsburgh, PA, USA) and an oxygen electrode (Orion Research, Boston, MA, USA). Hardness and alkalinity were measured by titration using kits from CHEMetrics (Calverton, VA, USA). The oxygen content of the sediment was not measured but a typical light brown oxic layer of sediment of approximately 3 to 5 mm was observed. Further, the concentration of contaminant in the overlying water was not measured but the frequent water exchanges were expected to keep the overlying water concentration low. On experimental days 1, 2, 7, 10, 17, and 28, the animals and sediment from three beakers of each size class were sampled for compound concentration and sediment wet to dry ratios (Kane Driscoll *et al*. 1997). The number of dead animals in each sampled beaker was recorded, and the animals from the 19th beaker were analyzed for lipid content on day 28.

As the data were analyzed, animals were placed into the size class indicated by their actual wet weight. Uptake rate coefficients (k_s) for most experiments were calculated using the 2-compartment model (Landrum *et al*. 1992b):

$$C_a = \frac{k_s C_s}{k_e}(1 - e^{-k_e t}) \quad (4)$$

where C_a is the concentration of compound in the animal (ng/g), k_s is the uptake coefficient (g dry sediment/g organism/h), C_s is the sediment concentration (ng/g dry sediment), and k_e is the elimination rate constant (1/h) determined from the elimination experiments. Compound availability appeared to decline over the course of the experiments for MCBP and DCBP at 16°C. This decline in compound availability was included in the calculation of k_s values for these compounds by using the following model (Landrum 1989):

$$C_a = \frac{k_s C_s^{t=0}}{k_e - \lambda}(e^{-\lambda t} - e^{-k_e t}) \quad (5)$$

where λ is the rate at which compound availability decreased.

The data for HCBP at 12°C with large animals were best represented by a linear model that assumes elimination is unimportant (Landrum *et al.* 1992b). Attempts to fit the data by other models were unsuccessful.

Field Comparisons of BSAF Values

Sediments and organisms collected from Lake Michigan were analyzed to determine BSAFs for animals in the field. Sampling, extraction, cleanup, and quantitation of sediment contaminants were conducted using methods that are compatible with and generally follow procedures outlined in the EPA's Lake Michigan Mass Balance Study Methods Compendium (Van Hoof and Hsieh 1997a,b). Sediment and animals samples were thawed at 4°C for 24 h and then brought up to room temperature. Animals were homogenized by mortar and pestle, and sub samples were removed to determine lipid content and wet-to-dry ratios. For PCB analysis, wet sediment (20 g) or animals (0.921 g) were dried with sodium sulfate and extracted with 150 mL methylene chloride. PCB congeners 65, 14, and 166 were added to the samples as surrogate standards for contaminant recovery determination. Samples were then sonicated for 1 h in a 30°C sonication bath. The extracts were allowed to equilibrate at this temperature for 24 h after which they were sonicated again for 1 h. After filtration through glass wool, extracts were concentrated by rotary evaporation followed by nitrogen gas blow-down. Methylene chloride was solvent exchanged with hexane, and extract clean-up was performed using columns containing 3 g of 3% deactivated silica gel overlaid with 10 g of 10% deactivated alumina. The PCB fraction was eluted with 35 mL of hexane. Gas chromatographic analysis of PCBs was performed on a Hewlett-Packard Model 5890 Series II equipped with an electron capture detector (GC/ECD) and a 60 m DB-5 fused silica capillary column (J&W Scientific, Folsom, CA).

Sixty-nine congeners or congener groups passed a quality control screen for use in the bioaccumulation comparison. Quality control parameters recorded on all samples include the collection of field blanks, duplicate or replicate sample collection, and surrogate injections into each sample. All samples were quantified using multiple internal standards. Several congeners were excluded from data analysis since they were below the method detection limits. Other values that were excluded from analysis include: five that had failed matrix spike recoveries, nine with blanks problems, and nine that exhibited interference from another compound. The results reported have been corrected for surrogate recoveries (69 to 91%).

Statistics

Linear regressions were performed using the statistical package, SYSTAT (SPSS, Chicago, IL), and the regression package in Scientist (MicroMath, Salt Lake City, UT). Differences between slopes or means were compared using a *t*-test also performed on SYSTAT. Power analyses were performed on the slope of regression lines according to Cohen (1977). Differences were considered significant when $p < 0.05$.

RESULTS

The data for this paper have been reported in a NOAA Technical Memorandum (Landrum *et al.* 1998, see http://www.glerl.noaa.gov/pubs/techrept/techrept.html TM-106). The technical memorandum contains additional details on the quality control for the study and all of the individual rate coefficients. This paper provides the analysis and interpretation of the data.

Selection of the temperature conditions for this study were based on the observed environmental range and tolerance of the organism. *Diporeia* has been observed to be present up to temperatures of

TABLE 1. Effect of temperature and organism size (mass) on the uptake coefficient from aqueous exposures from a linear regression of the following form: k_u = A* temperature (°C) + B* mass (mg) + C and the significance of each parameter in the regression as well as the overall regression.

Compound	Temperature Range	A	B	C	Adjusted R^2 and p value
MCBP	4–12°C	4.5 ± 1.6 p < 0.01	–4.1 ± 2.6 p = 0.12	146 ± 17 p < 0.001	0.063 p < 0.05 n = 109
DCBP	4–12°C	18.4 ± 2.7 p < 0.001	–19.5 ± 4.5 p < 0.001	232 ± 32 p < 0.001	0.399 p < 0.001 n = 111
TCBP	4–16°C	23.4 ± 1.1 p < 0.001	–18.1 ± 2.5 p < 0.001	21 ± 17 p = 0.22	0.771 p < 0.001 n = 158
HCBP	4–16°C	2.1 ± 1.5 p = 0.16	–15.5 ± 2.2 p < 0.001	274 ± 23 p < 0.001	0.286 p < 0.001 n = 156

23°C in the field and southern Lake Michigan organisms are tolerant of temperatures up to 26°C in the laboratory (Landrum and Nalepa 1998). However, 16°C was selected as an upper limit as it is close to the maximum temperature expected for 45 m stations (McCormick 1990). Thus, this was chosen to approximate a realistic upper limit for organisms for comparison with field data for organisms collected from the same station.

Accumulation from Water

To study the impact of size directly, a mass balance model with initial rates assumptions and a single time point for sampling was selected for the study. For the estimates of the uptake to be reflective of the organism then several assumptions need to hold. First, over the duration of the exposure elimination is unimportant, second the rate coefficients are constant, and finally no biotransformation occurs. The first assumption that the elimination is unimportant during the exposure is supported because the organism is just becoming loaded with the compound and the concentrations have not yet reached a level where elimination plays a substantial role. In the worst case MCBP at 12°C, which showed the greatest elimination rate constant, only about 33% of one half-life occurs during the uptake exposure. In all other cases, the elimination is much slower so there should be less influence of the elimination processes. If elimination is accounted for in this worst case using a model similar to equation 5 but using the water concentration as the source, the measured change in water concentration to provide the estimate for lamda, and the measured elimination rate constant, the estimate for k_u is within 3.3% on average of the values obtained from the mass balance model. This is substantially less variability than for the measured k_u values for a particular size organism (Table 1). Thus, it appears that the assumption that elimination is unimportant for this experimental design is appropriate. For the second assumption, there is really no way to test the validity that the uptake rate coefficient remains constant; this is true no matter what kinetic model is used. For the third assumption, the biotransformation of *Diporeia* is not measurable for PAH (Landrum 1988) and thus no metabolism of PCB congeners is expected. Finally, for a mass balance model, the contaminant is assumed to only be in the water or in the organism, since the bottles were allowed to equilibrate over night any sorption to the glass should have occurred prior to adding the organisms. The fact that recalculating the uptake based on water concentrations results in essentially the same k_u values for the worst case as described above, the mass balance model is producing reasonable estimates of the uptake for these PCB congeners.

The influence of organism mass and temperature on the uptake rate coefficients (k_us) of the PCB congeners was examined through multiple linear regression. With specific exceptions (discussed below), k_u increased with increasing temperature and decreased with increasing mass (Table 1). The data for MCBP (Fig. 1a) and DCBP (Fig. 1b) at

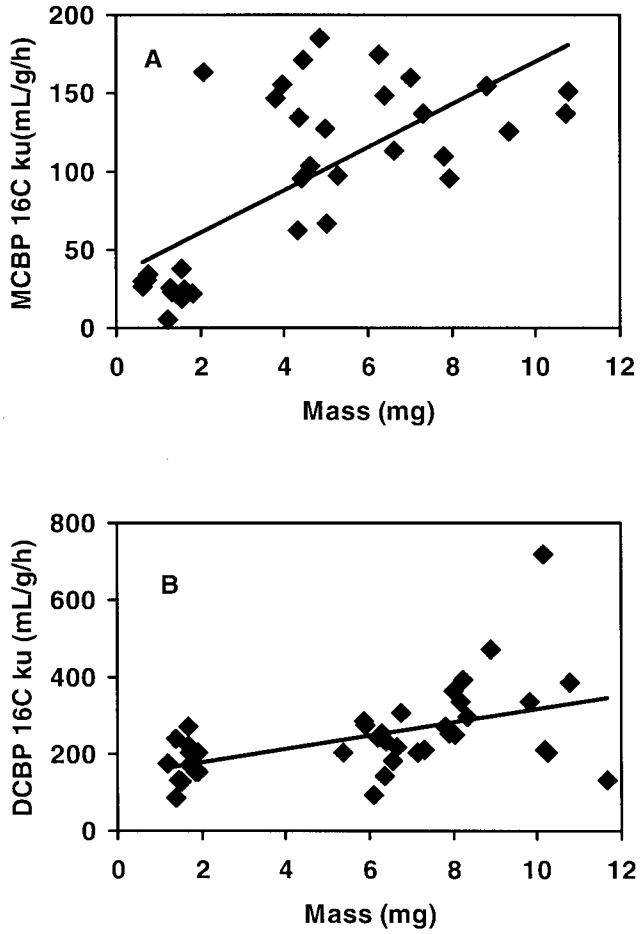

FIG. 1. a) Relationship between the uptake coefficient from water and the size (mass) of the* Diporeia *at 16°C for 4-chlorobiphenyl (MCBP). b) Relationship between the uptake coefficient from water and the size (mass) of the* Diporeia *at 16°C for 4,4′-dichlorobiphenyl (DCBP).

16°C were not used in the regression because k_u increases with increasing organism size suggesting a potential shift in mechanism for the rate-limiting step in accumulation. Data for MCBP and HCBP were exceptions to the general trend since organism mass had no influence on the uptake of MCBP and the relationship between temperature and uptake of HCBP was not significant (Table 1). Despite the significance of the overall regression for MCBP, the model only accounts for a very small part of the variance in the data. This primarily results from the absence of organism size as determinant in the accumulation process.

To examine the effect of hydrophobicity on the uptake rate coefficient, log K_{ow} was included as an additional independent variable in the multiple linear regression. This regression employed the data for all the compounds performing multiple linear regression using mass, temperature, and log K_{ow} as independent variables. The resultant regression was not significantly different from a regression that only included mass and temperature. There was no appreciable improvement in the r^2, 0.204 versus 0.198 with and without log K_{ow} or in the residuals for the two regressions. Thus, for the uptake process from water, the hydrophobicity of the PCB congener did not appear to affect the accumulation process. This result is different than was observed for polycyclic aromatic hydrocarbon accumulation by *Diporeia* where the uptake rate coefficient was directly proportional to the hydrophobicity of the specific congener (Landrum 1988).

Elimination

The elimination rate constants were determined for size classes of *Diporeia* (small, medium, and large as previously defined) since the elimination could not be determined for individual organisms. In order to accurately estimate elimination rate constants, the organisms at the beginning of the elimination phase must have the storage pools in the organism in dynamic equilibrium. For *Diporeia,* the various lipid pools are equilibrium with each other after 24 h (Gardner *et al.* 1990). Thus, measurements of elimination after only a 24 h loading phase should permit reasonable estimates of elimination. When elimination was estimated from a 28 d sediment uptake experiment for TCBP and HCBP (Landrum and Faust 1991), the elimination rate constants were similar to those found under this experimental design.

The elimination rate constants (k_e) for MCBP and DCBP were significantly different from zero for all size classes at all temperatures (Table 2). A significant rate of elimination of TCBP was determined for the small animals at 12 and 16°C, for the medium animals at all temperatures, but never for the large animals. A significant rate of elimination for HCBP was determined only for medium animals at 12°C (Table 2). Given the variability in the elimination data, the slope of the regression of ln C_a versus time should be detected at a slope of 0.0005/h with $p < 0.05$ with a power of 0.5. Thus, the elimination data for HCBP was at the limit of detectability for determining k_e.

In general, elimination rates were significantly

TABLE 2. BSAF Estimates of PCB Congeners in* Diporeia *spp. from toxicokinetics measurements.

Temperature Organism Size	k_s (g/g/h)	k_e (1/h)	% lipid	BSAF
MCBP				
4°C Small	0.015	0.0074	11.6	0.286
4°C Small	0.015[a]	0.0074	11.6	0.286
4°C Medium	0.019	0.0078	23.6	0.17
4°C Large	0.017	0.0031	25.1	0.36
8°C Small	0.025[a]	0.0081	11	0.459
8°C Medium	0.017	0.0061	19.4	0.23
8°C Large	0.0168	0.0058	24.5	0.19
12°C Small	0.025[b]	0.0098	8.1	0.515
12°C Medium	0.028[b]	0.008	14.3	0.407
12°C Large	0.021[b]	0.0046	19.2	0.389
16°C Small	0.025[a]	0.0019	7.8	2.759
16°C Medium	0.019	0.0026	18.3	0.653
16°C Large	0.013	0.0032	17	0.391
DCBP				
4°C Small	0.013	0.0055	12.2	0.317
4°C Small	0.018[a]	0.0055	12.2	0.439
4°C Medium	0.010	0.0035	21.7	0.215
4°C Large	0.0069	0.0015	27.8	0.271
8°C Small	0.014	0.0033	13.6	0.51
8°C Medium	0.011	0.003	18.5	0.324
8°C Large	0.009	0.0021	25.8	0.272
12°C Small	0.018	0.0059	7.8	0.640
12°C Small	0.037[a]	0.0059	7.8	1.32
12°C Medium	0.025	0.0045	15.7	0.579
12°C Large	0.014	0.0036	18.1	0.351
12°C Large	0.016[a]	0.0036	18.1	0.401
16°C Small	0.021	0.012	7.7	0.372
16°C Small	0.045[a]	0.012	7.7	0.797
16°C Medium	0.031	0.0036	17.8	0.791
16°C Large	0.016	0.0036	17	0.810
16°C Large	0.016	0.0019	17	1.535
TCBP				
4°C Small	0.012[a]	0.00098[c]	11.2	1.788
4°C Small	0.0016	0.00098[c]	11.2	2.384
4°C Medium	0.0039	0.00098	16.4	0.397
4°C Large	0.0038	0.00098[c]	18.5	0.343
8°C Small	0.017	0.00076[c]	9.6	3.811
8°C Medium	0.013	0.00076	18	1.554
8°C Large	0.0085	0.00076[c]	16.8	1.089
12°C Small	0.022	0.0011	8	4.089
12°C Medium	0.0087	0.0011	10.4	1.244
12°C Large	0.0049	0.0011[c]	16.1	0.453
16°C Small	0.033	0.0015	8.9	4.043
16°C Small	0.034[a]	0.0015	8.9	4.166
16°C Medium	0.025	0.0008	13.9	3.677
16°C Medium	0.026[a]	0.0008	13.9	3.824
16°C Large	0.017	0.0008[c]	15.3	2.272
16°C Large	0.022[a]	0.0008[c]	15.3	2.940

(Continued)

TABLE 2. Continued.

Temperature Organism Size	k_s (g/g/h)	k_e (1/h)	% lipid	BSAF
HCBP				
4°C Small	0.019	0.00058[d]	9.8	5.468
4°C Small	0.019[a]	0.00058[d]	9.8	5.468
4°C Medium	0.0072	0.00058[d]	13.8	1.471
4°C Large	0.0057	0.00058[d]	19.1	0.842
8°C Small	0.031	0.00058[d]	9.5	9.203
8°C Medium	0.017	0.00058[d]	17.2	2.787
8°C Large	0.0093	0.00058[d]	18.4	1.425
8°C Large	0.017[a]	0.00058[d]	18.4	2.606
12°C Small	0.031	0.00058[d]	8.9	9.823
12°C Small	0.039[a]	0.00058[d]	8.9	12.358
12°C Medium	0.014	0.00058[d]	13.9	2.840
12°C Large	0.008	0.00058[d]	15.3	1.475
12°C Large	0.022[a]	0.00058[d]	15.3	4.055
16°C Small	0.059	0.00058[d]	8	20.799
16°C Medium	0.02	0.00058[d]	11.4	4.948
16°C Large	0.019	0.00058[d]	15.5	3.457

[a]These values were determined in 1996. All other values were measured in 1995.
[b]These values represent the average of respective size classes from 8 and 16°C temperatures because the 12°C data was considered unreliable.
[c]Estimates of the elimination rate constant for calculation of BSAF were taken from the next larger or smaller size class at the same temperature that had a measurable value. From Figure 2, compounds with large log K_{ow} values show little influence of size on the elimination coefficient.
[d]Estimates for the elimination rate constant for hexachlorobiphenyl were taken from the estimates determined from the regression equations established for the small and medium animals in Figure 2.

larger for small animals in comparison to large animals. With some exceptions (described below) elimination rates were not significantly different between small and medium animals or between medium and large animals, although comparisons for TCBP and HCBP were limited because of limited data. Similarly, rates of elimination of individual compounds by a particular size class were generally not different at temperatures in the range of 4 to 12°C. However, elimination rates at 16°C were often smaller for MCBP and DCBP compared to other temperatures (Table 2).

Because of the limited range of data and the failure of the method to permit significant measurement of the elimination rate for HCBP, literature data for biphenyl and 2,2′,5,5′-tetrachlorobiphenyl (Landrum 1995) was used to increase the database to examine the relationship between k_e and log K_{ow}. Further, because the elimination rates were not significantly different between small and medium animals or for temperatures between 4 and 12°C, these data were pooled for a comparison of elimination versus log K_{ow} (Fig. 2). The elimination rates for the large animals using the pooled temperature data were examined separately (Fig. 2). The elimination rate coefficient for HCBP (0.00058/h for small and medium amphipods and 0.00055/h for large) was estimated from the regressions of k_e versus log K_{ow}. These values are not significantly different. It is interesting that the differences between the small and medium and large animals are most evident for compounds with smaller log K_{ow} values. If the data (Table 2) from each individual temperature were used independently in a regression model to estimate the elimination of HCBP, the estimated values would range from 0.00025 to 0.00054/h for the small and medium animals from 4 to 12°C.

Because the data for 16°C was different from that for the lower temperatures (Table 2), estimation of k_e for HCBP was performed separately. The k_e values were in general smaller than at the lower temperatures, primarily for the compounds with the lower log K_{ow} values. If the available data are fit to an exponential curve, the estimate of k_e for HCBP

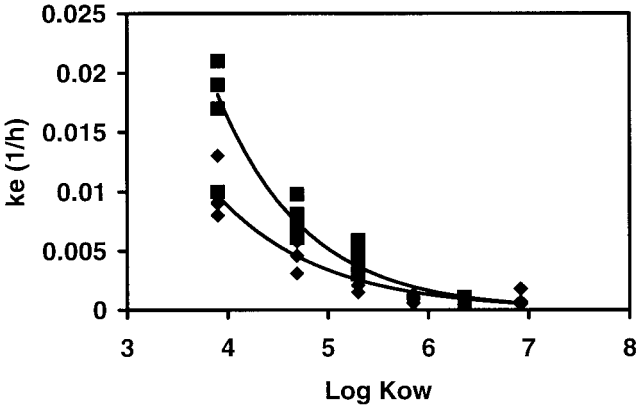

FIG. 2. The relationship between the elimination rate constant (k_e) and log octanol-water partition coefficient (log K_{ow}) for the small and medium size classes (■, $k_e = 1.56e^{-1.14 \log Kow}$) and for the large size class (◆, $k_e = 0.395e^{-0.952 \log Kow}$) for elimination coefficients measured between 4 and 12°C.

is 0.0008/h, which is somewhat larger than that estimated for the lower temperatures. However, the data are not as robust at 16°C as at the other temperatures, and the estimate for HCBP is not statistically different from that estimated in the range of 4 to 12°C.

Accumulation from Sediment

Because *Diporeia* are infaunal amphipods, their exposure is more to the sediment and interstitial water than to overlying water. The relatively frequent overlying water exchanges should have insured that the *Diporeia* received their dose directly from sediment in these experiments. This is further supported from observations that there were no differences observed in the uptake of selected sediment-sorbed polycyclic aromatic hydrocarbons by *Diporeia* whether the exposures were static or under flow-through conditions (Landrum 1989).

The field concentration of total PCB in the sediments prior to experimental use was 16.95 µg/kg based on the chemical analysis. Thus, the total PCB concentration is similar to the concentration of the individual congeners added for toxicokinetics. However, the added congeners are at least 20 times greater concentration than any specific congener in the PCB mixture. Since compounds appear to have independent action for accumulation at low concentrations such as these (Landrum 1989), the accumulation rates based on the radiolabeled compounds should be representative of what occurs in the field.

Most of the accumulation data for PCB congeners were collected during the summer of 1995 with some repeat and additional data collected in 1996. The data between the 2 years for the same organism's size, environmental temperature, and congener were generally similar (Table 2). The organic carbon content for this sediment averaged 0.44 ± 0.11% organic carbon (n = 84) on a dry weight basis. Animal mortality during the course of the sediment exposures was generally low, but showed a significant increase as experimental temperatures rose from 2 to 3% at 4°C to 3 to 11% at 16°C for exposure to all compounds for all size classes.

For MCBP and DCBP measured sediment concentrations declined over 28 d an average of 25 ± 3.5% for DCBP and 24 ± 9% for MCBP. The λ value in the model accounts for the change in compound availability whether the compound disappears chemically or the bioavailability changes. For 4°C, λ tracked the chemical disappearance of the compound while at higher temperatures the bioavailability appeared to change faster than the chemical availability. The λ values ranged from 0.0004 to 0.044/h for MCBP and from 0.0002 to 0.006/h for DCBP. A more rapid change in the bioavailability compared to chemical extractability was also observed for PAH bioaccumulation by *Diporeia* from sediment (Landrum 1989).

This was the first effort to examine both the role of temperature and organism size on the process of contaminant uptake from sediment. For MCBP, there was no evidence of either a temperature or size relationship on the uptake process (Table 2). The uptake clearance rate at 12°C is approximately one order of magnitude lower than the rates at either higher or lower temperatures. This may have resulted from the fact that the sediment concentrations were 5 to 11 times greater in the 12°C study than for the other studies with MCBP (equivalent to about 3.5 times greater on a molar basis). At this concentration, a toxic response may have affected the uptake. Thus, the data for this temperature are considered unreliable. For DCBP, as with MCBP, temperature did not appear to influence the accumulation process. For all other compounds, there were trends of increasing accumulation with increasing temperature (Table 2). In most cases, there was a significant linear regression with temperature for each size class that produced a Q_{10} of 2.52 ±

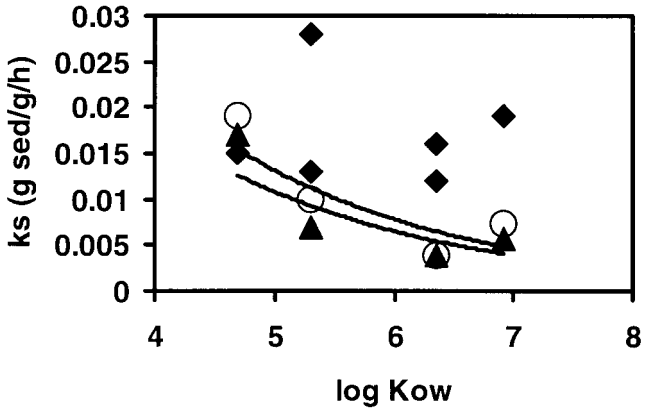

FIG. 3. Relationship between the uptake coefficient (k_s) from sediment exposures and log octanol-water partition coefficient (log K_{ow}) for all three size classes of organisms (small ◆, medium ○ upper trend line, and large ▲ lower trend line) at 4°C.

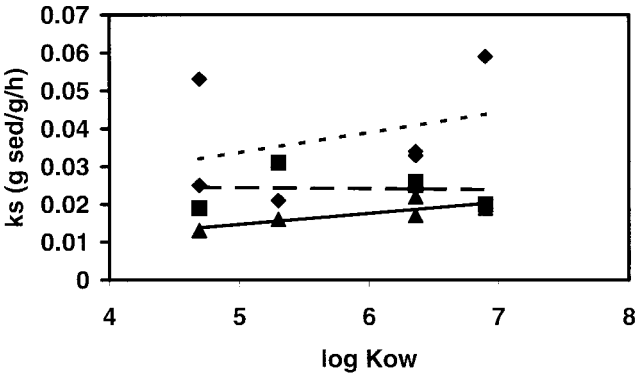

FIG. 4. Relationship between the uptake coefficient (k_s) from sediment exposures and log octanol-water partition coefficient (log K_{ow}) for all three size classes of organisms (small ◆ dotted line, medium ■ dashed line, and large ▲ solid line) at 16°C.

0.40, that is the rate increased approximately 2.5 times over a 10°C temperature range.

At 4°C, the uptake tended to exponentially decrease with increasing log K_{ow} (Fig. 3). This was mainly supported by the medium ($k_s = 0.18e^{-0.524 \log Kow}$, $r^2 = 0.64$) and large ($k_s = 0.14e^{-0.509 \log Kow}$, $r^2=0.65$) animals, while the data for the small animals were much more scattered and did not show any particular trend. Because of the small number of data points, these trends are not statistically significant. The trends were similar for the data at 8°C. However, at 12°C, the small animals exhibited an increasing uptake coefficient with log K_{ow}, while the medium and large animals had very scattered data with no apparent trend. Finally, at 16°C, the small and large animals show a slight trend of an increasing uptake coefficient with increasing log K_{ow} while the data for the medium sized animals are scattered (Fig. 4) only the trend for the large animals is statistically significant. Thus, at the higher temperatures, there is very little dependence of the sediment uptake coefficient on the octanol water partition coefficient and what small dependency occurs exhibits a positive trend with log K_{ow}.

Lipid Content

In addition to measuring uptake coefficient in the sediment exposures, the lipid content was determined for each group of organisms at the beginning and end of the sediment uptake studies. The lipid content within each size class did not change over the course of the exposures. However, for smaller animals the lipid content tended to be lower after acclimation to the increasing exposure temperatures. Correlations of lipid versus dry weight for each temperature yielded apparently linear correlations (Fig. 5). The slopes of the regression lines were similar and ranged from 7.2 to 9.2% lipid/mg dry weight while the intercepts tended to decline from 13.2 to 5% lipid over the range of temperatures 4 to 16°C.

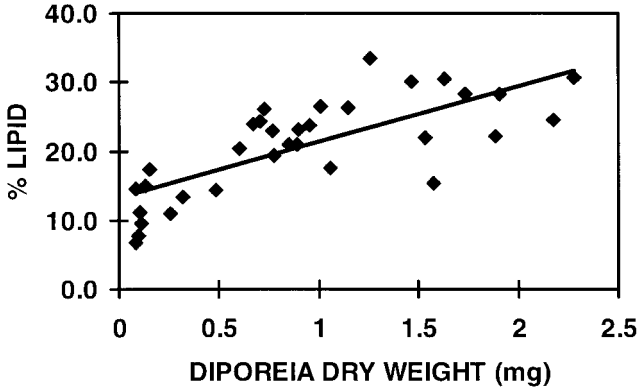

FIG. 5. The relationship between the lipid composition (%lipid on dry weight basis) and the size of* Diporeia *determined for the experiment with DCBP at 4°C.

Biota-sediment Accumulation Factors

BSAF (lipid normalized organism concentrations divided by carbon normalized sediment concentration) were determined from the steady-state limit of the sediment accumulation model:

$$\frac{dC_a}{dt} = k_s C_s - k_e C_a \quad (6)$$

where C_a = concentration in the organism, C_s = concentration in the sediment, k_s = the uptake coefficient from sediment exposures and k_e = the elimination rate constant.

At steady state, the bioaccumulation factor (BAF) is calculated from the kinetics

$$BAF = \frac{C_a}{C_s} = \frac{k_s}{k_e} \quad (7)$$

and then converted to a BSAF by correcting to the relative amount of lipid in the *Diporeia* and organic carbon in the sediment. For *Diporeia*, the lipid was measured on a dry-weight basis and the kinetics on a wet-weight basis, so an additional factor for the dry-to-wet weight ratio needed to be incorporated, 0.269 (Landrum 1988).

The BSAF values were calculated for each compound in each size class at each temperature (Table 2). This incorporates all the known information about the effect of size and temperature on the data. Because some data were missing or unreliable, estimates of several kinetic values had to be made in order to calculate the BSAF values for certain compounds at certain temperatures. For, MCBP at 12°C, the uptake coefficients from sediment for each size class were set at the average for that size class determined at the other temperatures since the 12°C data were considered unreliable. This approach could be used because of the general absence of temperature effects on the kinetics for MCBP. For HCBP, a predicted elimination constant was employed. For TCBP, the measured elimination constant for the large animals and some small animals was set equal to that for the medium animals. Because the elimination data do not suggest large distinctions among size classes for the very hydrophobic compounds, average lipid values for the respective size classes were used. Average values for sediment organic carbon were also used. The relationship between log K_{ow} and the BSAF was exponential at each temperature and the medium and large animals had little spread in their BSAF values (Table 2). The small animals were much different from the medium and large animals and exhibited very high BSAF values (Table 2). A model of BSAF versus log K_{ow} and temperature was explored with the following form:

$$BSAF = aTemp + be^{log\ Kow} \quad (8)$$

The large and medium sized animals were combined to form one model because the data were not particularly different and because this is the range of organisms that was used for the analysis of field samples. The small animals were analyzed separately.

Medium and large animals

$$BSAF = 0.057\ (0.018)\ Temperature + 0.0019\ (0.0003)e^{log\ Kow} \quad (9)$$

$r^2 = 0.80$, n = 38

Small animals

$$BSAF = 0.0096(0.046)\ Temperature + 0.0074(0.0008)\ e^{log\ Kow} \quad (10)$$

$r^2 = 0.87$, n = 23

Numbers in parentheses represent standard errors from the regression. One outlier was eliminated from the regression for the small organisms, HCBP at 16°C. For the small animals, the temperature term is not significant and an equally good regression can be obtained without including temperature.

BSAF values from *Diporeia* and sediment taken directly from the field were plotted against log K_{ow} to determine the ability to predict the observed BSAF values. These animals were collected independently and sorted according to length. The size class was determined to be approximately equivalent to the medium and large animals from the kinetics study. Organisms collected in the fall of 1999 were sorted in the same manner as had been done for the field collections, and the mean wet weight was 7.7 ± 0.5 mg wet weight (Sander Robinson, Great Lakes Environmental Research Laboratory, Ann Arbor, MI, personal communication). Animals collected from a nearby site at the same time of year as the field sample for BSAF had an average wet weight of about 6 mg with a range of 4 to 8 mg (Landrum 1988). Thus, both estimates put the likely population for the field data in the medium to large size class. To make a prediction for comparison, a temperature needed to be selected. The measured values in late summer at the 45 m station where the

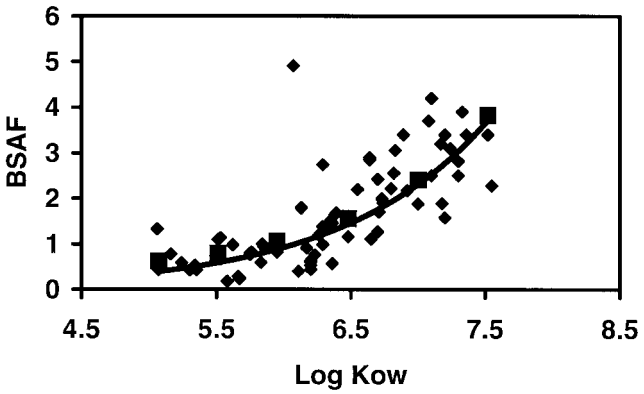

FIG. 6. Comparison of the BSAF values predicted from the toxicokinetics (■) and field measured values (◆) for* Diporeia. *The regression line is the least squares fit through the field data.

sediment and the organisms were collected ranges from 4.2 to 6°C with an average of 4.7 ± 0.6°C for values measured in July and August 1995 (Nathan Hawley, personal communication, Great Lakes Environmental Research Laboratory). When this temperature is selected, the predicted BSAF values essentially predict the trend line for the least squares fit of the field data (Fig. 6).

DISCUSSION

Accumulation from Water

The influence of organism mass and temperature on the water-only uptake coefficient (k_u) for PCB congeners was similar to that for polycyclic aromatic hydrocarbons (PAH) (Landrum 1988). In general, increasing mass resulted in decreasing k_u values. This suggests that, for most cases, the rate limiting step in the uptake process results from the rate of distribution within the organism, since mass is a surrogate for volume of the organism. Thus, increasing volume results in slower distribution to the storage site, presumably lipid. This may also reflect the generally greater surface-area-to-volume ratio for smaller organisms allowing faster uptake.

Accumulation of MCBP (log K_{ow} 4.5) at test temperatures below 16°C (4, 8, and 12°C) was not influenced by the mass of the organisms, which is consistent with what has been observed for phenanthrene (log K_{ow} 4.59) at 4°C (Landrum 1988). The consistent observations for compounds with moderate log K_{ow} values suggests that for the more hydrophilic compounds the role of internal distribution in the uptake kinetics is minimal resulting in minimal impact of size on the measured accumulation rates.

At 16°C, the greater uptake rate with increasing size, observed for MCBP and DCBP, suggests a completely different rate limiting step is responsible for the rate of accumulation. If distribution is not rate limiting, the capacity of the storage site may be influencing the rate of uptake. Larger animals have greater lipid content (Fig. 5) and this may govern the overall uptake.

As the compounds become more hydrophobic, the role of the internal distribution processes seems to become more and more rate limiting. When the compounds are sufficiently hydrophobic (log $K_{ow} \geq 6$), then increasing temperature does not overcome the internal distribution processes as the rate limiting step. This is consistent with the data where DCBP dependence on mass exhibits significant negative correlations with organism size for 12°C and lower. While at 16°C, the relationship has switched to exhibit a positive relationship with the organism size (Fig. 1b), again suggesting that the storage capacity of the organisms dominates the rate of accumulation. For the more hydrophobic compounds, TCBP and HCBP, the apparent rate limiting step remains distribution limited and does not change within the temperature range studied. The apparent changes in rate limiting steps as the compounds become more hydrophilic suggest that kinetic limitations are minimized and hydrophobic partitioning behavior is more important in the accumulation of these compounds. In addition to observing differences in the character of the compounds and the apparent rate limiting steps, the slopes of the correlations between k_u and mass are generally greatest at 8°C suggesting that the distribution process has the greatest impact on the rate compared to other competing processes at this temperature.

From the above, it is clear that temperature is important in controlling the physiology and ultimately the rate determining step in the accumulation process for aqueous exposures. For MCBP and DCBP, the uptake rate at 16°C is significantly lower than at 4°C for small organisms. If in fact the mechanism shifts to a storage capacity driven phenomenon, then there is apparently an impact on the presentation of the molecule to the surface at 16°C suggesting changes in respiration. Since these animals are cold water organisms, it is reasonable to expect that high temperatures such as 16°C could have an adverse effect that would reduce respira-

tion; although there are no data to support this speculation.

Unlike the PAH, which exhibited a positive linear response between log K_{ow} and uptake clearance from water (Landrum 1988), the uptake clearance of PCBs was not related to K_{ow}. Thus, steady-state accumulation of PCBs will be more related to the inverse relationship of the elimination rate to log K_{ow}. This is supported by the shape of the BSAF versus log K_{ow} curve (Fig. 6).

Comparing the results from this study with those from previous work could only be done for hexachlorobiphenyl at 4°C since that is the only compound for which a significant amount of data exists. The relationship between mass and uptake clearance was determined for the data in Landrum (1995) and in this work. The new data were more variable than the older data. The two regressions were similar with the new data yielding a somewhat flatter regression than the older data (Old: ln k_u = –129(17.1) mass(g) + 5.5(0.14), r^2 = 0.57; New: ln k_u = –68.1(33.8) mass (g) + 5.2(0.14); r^2 = 0.104). However, the slopes were not significantly different. Thus, the data from this work can be considered relatively invariant with time and reflect the characteristics of the organism.

Elimination

Elimination rate generally declined with the increasing size of the organisms (Table 2), a difference that was particularly apparent between the small and large *Diporeia* but not between small and medium organisms. The exponential relationship between log K_{ow} and k_e for small and medium animals (Fig. 2), including the data from previous work to expand the range of log K_{ow} (Landrum 1995), gives an exponential relationship that is similar to the one found for PAH (Landrum 1988). Thus, uptake is more dependent upon temperature than is elimination and elimination is more dependent upon the hydrophobicity of the contaminant.

The large animals over the 4 to 12°C range had lower elimination constants than the small to medium animals (Table 2). Again, apparently little response to temperature occurs over this range. However, as log K_{ow} increases, the regressions between the large and the medium and small *Diporeia* converge and little difference in elimination rates occurs. Apparently, surface area to volume ratios of the organisms are more important for elimination rate of the less hydrophobic compounds while elimination of more hydrophobic compounds, approximately log $K_{ow} \geq 5.5$, are apparently more limited by the resolubilization of the compound leaving the organism into the aqueous environment (Fig. 2).

In comparisons of size (mass), K_{ow}, and temperature, the data at 16°C were inconsistent with data collected at other temperatures. These differences may, in part, be due to the effect of thermal stress on the animals since mortality data from the sediment uptake study showed a significant increase in animal mortality as temperature increased in the sediment accumulation studies.

Uptake from Sediment

Both temperature and K_{ow} influence the accumulation process from sediment. The organic carbon content of this sediment is low (0.44%) but in the range where the organic matter content is expected to dominate the partitioning to the sediment in equilibrium partitioning considerations (DiToro *et al*. 1991). In this data set, the medium and large animals had very similar accumulation rates across the range of compounds studied and exhibited similar trends with K_{ow}. The most interesting feature is the relationship with log K_{ow} as the temperature increases. At lower temperatures, 4 and 8°C, the large and medium animals show a shallow decline in sediment uptake rate as reflected in the uptake coefficient with increasing log K_{ow} (Fig. 3). However, as the temperature is elevated the trend flattens, and at 16°C, there is a small upward trend in the uptake clearance (Fig. 4). This suggests a shift in the factors controlling the uptake of these compounds from the sediment. At the low temperatures, the uptake appears to be dominated by sorption to the sediment particles in a manner similar to that observed for PAH (Landrum 1989). Thus, the more hydrophobic the compounds, the more strongly they are bound to sediment and therefore less bioavailable. This suggests that desorption from sediment particles is an important step in the bioaccumulation process. Recent work demonstrated that desorption and uptake from interstitial water tended to dominate at low temperatures but that the ingestion route became more important as temperature increased due to increasing ingestion rates (unpublished data). Thus, the positive slope at the higher temperature supports the notion that the particle desorption rate no longer limits the kinetics. This is the first time that a temperature effect on the sediment uptake kinetics has been reported. Although, the exact mechanism limiting the uptake, particularly at higher temperatures, is not fully understood,

recent work suggests that the effect is linked to changes in feeding rate.

One of the surprising features in the uptake clearance data is the much greater uptake rate observed for the smaller amphipods. This is partially attributed to a faster feeding rate (feeding rate for the small size class is 9.8 ± 10.4 µg/mg/h while for medium and large animals the feeding rate is 2.4 ± 2 µg/mg/h at 4°C feeding on Lake Michigan sediment, unpublished data) although the exact mechanism remains to be investigated. In addition, there are likely differences in the selectivity of particles for ingestion by small amphipods compared to large amphipods. Since the relative contaminant distribution and absorption efficiency seem to vary with the particle size (Harkey *et al*. 1994), it is likely that both the selectivity and the rate of feeding would contribute to differences in uptake between the small and larger animals. In addition to the above two arguments, small animals also have greater surface-area-to-volume ratios which might contribute to an increase in uptake from the aqueous phase that was observed in the water-only studies.

Overall, assessing the accumulation of PCB congeners from sediments by *Diporeia* will need to be done on a size class basis. As with the elimination data, the data were not sufficiently resolved so that regression relationships with organism size could be performed since the rate constants had to be determined using multiple organisms. Other experimental designs that provide more detailed size dependent measures are needed to obtain improvements in the role of size on the accumulation from sediment.

Estimations of Exposure (Biota-Sediment Accumulation Factor)

The purpose of the kinetics measurements was to look for the potential to model (predict) the exposure of *Diporeia* to PCB congeners as a part of the U.S. EPA's Lake Michigan Mass Balance Program. Previous work had limited data on PCB congeners and the available data on accumulation had only been measured at 4°C. This work attempted to improve the database and allow an examination of these factors to produce a more predictable model.

The expectation is that organisms collected from the field will be at steady-state with respect to their exposure. However, because of changes in physiology with growth and temperature, there is an expectation that the steady-state condition will vary with changes in the size of the amphipods and the time of year, driven primarily by temperature and lipid content. To examine the potential to predict the bioaccumulation of PCB congeners two assumptions were made: 1) whole sediment concentrations reflect the exposure concentration in the external media, and 2) exposure to overlying water is not a significant contributing factor.

The shape of the relationship of BSAF versus log K_{ow} (Fig. 6) does suggest that the mechanism for accumulation is not simply passive partitioning as suggested by the Equilibrium Partitioning (EQP) Theory (DiToro *et al*. 1991). EQP predictions suggest that the BSAF should be a constant value invariant with log K_{ow} and in the range of 1.7 (McFarland 1984, McFarland and Clarke 1989). At small values of log K_{ow}, the BSAF is significantly lower, approximately a factor of 4, than would be expected from EQP theory and at the upper range of log K_{ow}, the BSAF exceeds that expected by EQP theory by approximately a factor of two. For the small size class of amphipods, the range of estimated BSAF values is even greater and is confirmed by the preliminary field data available from the Lake Michigan Mass Balance program (Hsieh *et al*. 1996). The data set truncates at log K_{ow} of 6.92 for the laboratory data. The range of log K_{ow} values in the field data exceeds that of the laboratory data and for compounds with very high log K_{ow} (> 7.5), the field BSAF decline (not shown). It is beyond the scope of the existing kinetics data to predict this feature. This model (equation 9) also suggests that the congeners are acting independently over the concentration range predicted. That is, the kinetics from exposure to individual congeners predicts the field data from exposures to the mixture of compounds existing in the sediment. It is likely that such independence could disappear if the concentration became high enough to produce toxic effects or there were strong chemical interactions. Finally, the shape of the BSAF versus log K_{ow} curve is exponentially increasing. This curve is different from that found by Morrison *et al*. (1996) for organisms in Lake Erie. However, those organisms were generally warm water species; this may account for some of the differences. It will be interesting to further examine the mass balance field data to see if the exponential form holds at more sites.

The ability to fit data from one station does not mean that the data from other stations can be fit with the same model. There are aspects about the impact of sediment composition that are not incorporated in the current work. Attempts to improve the modeling should incorporate information about

the effect of sediment composition on uptake. Once the impact of sediment composition on the bioavailable fraction of contaminant is better understood a more general model could be developed.

SUMMARY

Significant insight was gained in this study on the factors that influence the accumulation of PCB congeners by the amphipod, *Diporeia* spp. While good agreement was found between predicted and measured values in this one sediment, insufficient data are available to fully model the accumulation from sediment at this time because of the incomplete understanding of the differences in bioavailability among sediments. At a minimum, the accumulation kinetics from several different sediments at all temperatures and size classes would be required to obtain better estimates of the accumulation potential. However, it may be possible to develop a field-based model once the field analyses from the Lake Michigan Mass Balance study are complete.

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