COMPARISON OF THE UPTAKE OF POLYCYCLIC AROMATIC HYDROCARBONS AND ORGANOCHLORINE PESTICIDES BY SEMIPERMEABLE MEMBRANE DEVICES AND CAGED FISH (*CARASSIUS CARASSIUS*) IN TAIHU LAKE, CHINA

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Abstract—Uptake of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) by triolein-containing semi-permeable membrane devices (SPMDs) and by crucian carp (*Carassius carassius*) was studied in Taihu Lake, a shallow, freshwater lake in China. Crucian carp and SPMDs were deployed side by side for 32 d. The first-order uptake rate constants of individual PAHs and OCPs for the two matrices were calculated and compared to relate the amounts of chemicals accumulated by the matrices to dissolved water concentrations. On a wet-weight basis, total concentrations of PAHs and OCPs in crucian carp fillets averaged 49.5 and 13.6 ng/g, respectively, after the 32-d exposure, whereas concentrations in whole SPMDs averaged 716.9 and 62.3 ng/g, respectively. The uptake rate constants of PAHs and OCPs by SPMDs averaged seven- and fivefold higher, respectively, than those for crucian carp; however, the patterns of uptake rate constants derived from test chemical concentrations in the crucian carp and SPMDs were similar. Although equilibrium was not reached for some PAHs and OCPs during the 32-d exposure period, a reasonably good correlation between the concentration factors (CFs) and octanol/water partition coefficient (K_{ow}) values of PAHs and OCPs in SPMDs ($r = 0.86$, $p < 0.001$) was observed when potential sorption to dissolved organic carbon was taken into account. Similar efforts to correlate the CFs and K_{ow} values of PAHs and OCPs in crucian carp ($r = 0.75$, $p < 0.001$) were less successful, likely because of PAH metabolism by finfish. Overall, the present results suggest that SPMDs may serve as a surrogate for contaminant monitoring with fish in freshwater lake environments.

Keywords—Semipermeable membrane devices Dissolved organic carbon Bioconcentration Passive sampling

INTRODUCTION

Bivalve mollusks and finfish have been widely employed as biomonitoring organisms (BMOs) because of their ability to accumulate trace levels of many hydrophobic organic contaminants (HOCs) from environmental water columns. Residue levels in tissues of exposed BMOs generally are considered to represent time-integrated concentrations of targeted HOCs in the ambient environment. A number of factors, however, such as reproductive state, age, size, environmental conditions, and ability of some BMOs to metabolize certain HOCs, limit the use of aquatic organisms for monitoring chemical exposure. To avoid many of these limitations, in situ passive sampling devices, such as lipid-containing semipermeable membrane devices (SPMDs), have been developed [1] and used extensively in recent years [2–4]. The SPMDs are designed to sample the truly dissolved fraction by the thermodynamically driven process of solute partitioning [1,5] between the aqueous and lipid phases. In this respect, SPMDs mimic the bioconcentration process of HOCs in aquatic organisms [1,6]. Although the use of man-made SPMDs to complement or to replace BMOs may be valid to better meet the goals of many monitoring programs, their performance must be thoroughly tested relative to traditionally used BMOs under controlled laboratory conditions and in the field.

Many studies have been carried out comparing the accumulation of HOCs by SPMDs and by aquatic organisms (mostly bivalves) in coastal waters and freshwater rivers [2,7–9],

but few studies have been conducted to compare the uptake of HOCs (including persistent and readily metabolized compounds) by SPMDs and fish in shallow freshwater lakes. Freshwater lakes play a critical role in providing human populations with drinking water, agricultural irrigation, and recreational opportunities. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are important environmental contaminants because of their wide distribution and persistence in the environment and their mutagenic/carcinogenic potential [10,11]. Freshwater lakes often represent major sinks for these contaminants and high concentrations of some of these chemicals accumulate in fish via various environmental pathways. Given the common use of SPMDs and the crucial role of uptake rate constants in the estimation of dissolved concentrations of HOCs in water, surprisingly few reports with these types of data have appeared.

The objectives of the present study were to determine the uptake rate constants of some PAHs and OCPs in SPMDs and crucian carp (*Carassius carassius*) deployed in a representative freshwater lake and to examine how well the uptake of HOCs by SPMDs mimic that of fish. The ultimate goal was to provide information regarding the suitability of SPMDs as a surrogate for fish in monitoring for the presence and concentrations of HOCs in freshwater lakes. We chose Meiliang Bay, Taihu Lake, as our study site, because Taihu Lake is the third-largest freshwater lake in China and currently serves 33 million people. Furthermore, Meiliang Bay (at the northern tip of the lake) has relatively constant concentrations of PAHs and OCPs in the surface waters and sediments [12,13], and

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normally, variations of both temperature and flow/turbulence in the lake water are relatively small.

MATERIALS AND METHODS

Chemicals

Solutions of 16 priority pollutant PAH standards, 17 OCP standards, and both *cis*- and *trans*-chlordane were purchased from Supelco (Bellefonte, PA, USA). Standards (purchased from the same vendor) of phenanthrene- d_{10} , 2,4,5,6-tetrachloro-*m*-xylene, and polychlorinated biphenyl (PCB) 209 were used as surrogates, and standards of pentachloronitrobenzene and hexamethylbenzene were used as internal standards. Triolein (1,2,3-tri[(*cis*)-9-octadecenoyl]glycerol) of 95% purity was obtained from Sigma-Aldrich (St. Louis, MO, USA). Pesticide-grade organic solvents were obtained from Fisher Scientific (Fair Lawn, NJ, USA).

Study design and sample collection

The 1-ml triolein-SPMDs were prepared in the manner described by Huckins et al. [14]. The thickness of the low-density polyethylene membrane used ranged from 75 to 90 μm , and the ratio of the membrane surface area to triolein volume was approximately 450 cm^2/ml . Before deployment, SPMDs were stored in sealed, acetone-rinsed, stainless-steel containers at 4°C.

Crucian carp was selected as a BMO because it was widely distributed in the area around Taihu Lake. The adult crucian carp (weight, 180 ± 30 g; length, 22 ± 2 cm; mean $\pm$ standard deviation) used in the present study were obtained from the hatchery of the Freshwater Fisheries Research Center, Chinese Academy of Fishery Sciences (Wuxi, China), and were acclimated in the laboratory with dechlorinated tap water for at least one week before use. The water temperature was $20 \pm 2^\circ\text{C}$, and the fish were not fed during the acclimation period.

Field exposures were carried out for 32 d in the year 2004 (from mid-June to mid-July). Before the field exposure, three acclimated fish were captured and used as reference samples to determine the background levels of target compounds in wet, whole-body tissue. At the field site, 25 fish were placed in a stainless-steel cage ($\sim 1 \times 1 \times 1$ m), which was submerged in the water column (depth, 2 m) and fixed on a stake at the sampling site in the Meiliang Bay. All the fish were visually examined before initiation of the exposure and found to be in good condition. Concurrently, 15 SPMDs were mounted on a wood rack, which was deployed near the fish cage. Fish were not fed during the exposure, and as such, they relied on naturally available food items during this period.

The water temperature at the site varied from approximately 19 to 23°C during the exposure period. The average linear velocity of water at the deployment site was estimated as approximately 5 cm/s. Field blank SPMDs [15] were exposed to the atmosphere at the site during the interval of time required for deployment and retrieval, then placed back in their containers and returned to the laboratory. These field blanks were used to determine any potential airborne contamination.

Three SPMDs and five fish each were sampled at days 4, 8, 16, and 32 of the exposure. The fish were transported to the laboratory, where muscle tissues (fillets) were isolated and stored at -20°C until analysis. After retrieval, most surficial material was removed from SPMDs directly using ambient water from the site. Before analysis, the SPMDs were stored in sealed glass jars at a temperature of 4°C. Samples of surface

water (2 L) also were collected at each sampling time and preserved in amber glass containers at 4°C; extraction was performed within 7 d.

Sample extraction and cleanup

The SPMDs were cleaned in the laboratory by scrubbing in distilled water, dipped in hexane and 1 M HCl, and were then rinsed briefly with acetone and isopropanol. Individual SPMDs were dialyzed twice for 24-h periods in separate 200-ml volumes of hexane at 18°C. The dialysates were combined and preconcentrated to 1 ml by a rotary evaporator (Büchi, Flawil, Switzerland).

Approximately 12 g of wet muscle tissue were dissected from each fish, homogenized, and dried with preextracted sodium sulfate. Each sample was spiked with the surrogate standards (2,4,5,6-tetrachloro-*m*-xylene and PCB 209 for OCPs and phenanthrene- d_{10} for PAHs). These samples were extracted with 200 ml of hexane/acetone (50:50, v/v) in a Soxhlet apparatus. The extracts were concentrated to 1 ml and solvent-exchanged into hexane.

Samples of surface water also were spiked with the same surrogate standards and filtered through 0.45- μm glass-fiber filters (Millipore, Billerica, MA, USA). The water samples were extracted by C_{18} cartridges. After extraction, the C_{18} cartridge was eluted with 10 ml of dichloromethane, and the extracts were reduced by N_2 blow-down to a final volume of 1 ml and the solvent exchanged to hexane.

All the sample extracts were then cleaned with column chromatography (inner diameter, 10 mm) using 8 g of alumina/silica gel (1:2, w/w) and 70 ml of dichloromethane/hexane (30:70, v/v) as eluent. Eluants were evaporated and solvent-exchanged into hexane. An appropriate amount of internal standards (hexamethylbenzene for PAHs and pentachloronitrobenzene for OCPs) were added to the final extract before instrumental analysis.

Instrumental analysis

Analysis of OCPs was carried out with an Agilent (Santa Clara, CA, USA) 6890 series gas chromatograph equipped with a ^{63}Ni electron-capture detector. Details of the OCPs analysis have been described elsewhere [16]. The PAHs were analyzed using an Agilent 6890 series gas chromatograph equipped with an Agilent 5973 Network mass-selective detector and a 60-m DB-5 MS silica fused capillary column. Detection was performed using selected-ion mode, and the details of other instrument conditions and quantitation have been reported elsewhere [13]. Finally, filtered lake water samples ($n = 3$) were analyzed with a total organic carbon (TOC) analyzer (TOC-5000, Shimadzu, Tokyo, Japan).

Quality control and assurance

Laboratory quality-control procedures included analyses of method blanks (solvents), spiked blanks (standards spiked into solvent), and matrix spikes (standards spiked into clean water, fish tissue, and unexposed SPMD). These samples were routinely analyzed with field samples. Surrogate standards were added to all the samples to monitor matrix effects. The recoveries of surrogate standards fell within a fairly narrow range (75–91%). The average recoveries of PAH and OCP mixtures in matrix spikes were from $54.7\% \pm 6.4\%$ to $94.3\% \pm 5.2\%$ and from $44.6\% \pm 0.9\%$ to $102.1\% \pm 2.2\%$, respectively. Concentrations of PAHs and OCPs reported herein were corrected using the recoveries of surrogate standards. The method

Table 1. Concentration of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water, semipermeable membrane devices (SPMDs) and crucian carp (*Carassius carassius*) and comparison of 32-d PAH concentration factors determined in the present study to similar values reported in the literature

Compounds ^a	Log K_{ow} ^b	Water concentration		SPMDs ^d (ng/g SPMD)	Crucian carp ^d (ng/g wet wt)	Log concentration factor			
		Whole (ng/L)	Dissolved ^c (ng/L)			Present study ^e		Huckins et al. [17] ^f	
						Crucian carp	SPMDs	Oysters	SPMDs
PAHs									
Naphthalene	3.5	92.4	92.4	101.3	10.6	2.1	3.0	1.9	3.2
Acenaphthylene	4.1	10.1	10.1	17.8	2.1	2.3	3.2	2.4	3.7
Acenaphthene	4.2	5.7	5.7	22.0	1.0	2.2	3.6	2.7	3.8
Fluorene	4.4	7.7	7.7	28.7	1.8	2.4	3.6	2.9	3.9
Phenanthrene	4.5	12.6	12.4	68.3	7.8	2.8	3.7	3.3	4.0
Anthracene	4.5	3.9	3.8	20.2	1.9	2.7	3.7	3.4	4.0
Fluoranthene	5.2	17.3	15.9	181.3	9.0	2.8	4.1	3.8	4.0
Pyrene	5.3	12.1	10.9	141.7	5.8	2.7	4.1	3.9	4.0
Benz[<i>a</i>]anthracene	5.9	2.5	1.7	21.9	1.5	2.9	4.1	—	—
Chrysene	5.6	2.1	1.7	12.6	1.2	2.8	3.9	3.6	3.9
Benzo[<i>b</i>]fluoranthene	5.8	4.1	3.1	36.7	1.8	2.8	4.1	3.8	3.9
Benzo[<i>k</i>]fluoranthene	6.2	2.2	1.2	11.8	0.9	2.9	4.0	3.6	3.8
Benzo[<i>a</i>]pyrene	6.4	2.1	0.9	13.5	0.7	2.9	4.2	3.6	3.9
Dibenz[<i>a,h</i>]anthracene	6.8	ND ^g	ND	16.2	1.3	—	—	3.3	3.9
Indeno[1,2,3- <i>cd</i>]pyrene	6.5	ND	ND	7.3	0.8	—	—	3.5	4.0
Benzo[<i>ghi</i>]perylene	6.9	ND	ND	15.5	1.3	—	—	3.4	3.9
ΣPAHs		172.7	167.6	716.9	49.5	—	—	—	—
OCPs									
α-Endosulfan	3.6	0.65	0.65	0.6	0.1	2.2	3.0	—	—
γ-HCH	3.7	4.09	4.09	1.5	0.5	2.1	2.6	—	—
β-HCH	3.8	7.81	7.81	4.2	1.4	2.3	2.7	—	—
α-HCH	3.8	4.79	4.79	5.1	0.4	1.9	3.0	—	—
δ-HCH	4.1	0.88	0.88	1.7	0.2	2.3	3.3	—	—
Heptachlor epoxide	5.0	0.08	0.08	0.4	0.1	3.1	3.8	—	—
Heptachlor	5.3	0.42	0.38	4.8	1.2	3.5	4.1	—	—
Hexachlorobenzene	5.5	0.95	0.81	23.6	4.2	3.7	4.5	—	—
4,4'-DDD	5.5	0.38	0.32	9.8	2.3	3.9	4.5	—	—
4,4'-DDE	5.7	0.29	0.24	7.4	2.2	4.0	4.5	—	—
<i>cis</i> -Chlordane	5.9	0.16	0.11	0.8	0.2	3.3	3.9	—	—
<i>trans</i> -Chlordane	6.1	0.14	0.08	1.9	0.6	3.9	4.4	—	—
4,4'-DDT	6.2	0.09	0.05	0.4	0.1	3.1	3.9	—	—
ΣOCPs		20.7	20.30	62.3	13.6				

^a HCH = hexachlorocyclohexane; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenylethane.

^b K_{ow} = octanol/water partition coefficient. Selected values are from Mackay et al. [34,35].

^c Corrected for 5 mg/L of dissolved organic carbon and the assumption $K_{DOC} = 0.11K_{ow}$.

^d Mean values ($n = 3$ for SPMD and $n = 5$ for crucian carp).

^e Values are based on dissolved concentrations.

^f Values are from the 250 ng/L treatment.

^g ND = not detectable.

detection limits of OCPs for water, SPMD, and fish samples were 0.06 to 0.5 ng/L, 0.3 to 1.8 ng/g (wet wt), and 0.08 to 1.3 ng/g (wet wt), respectively. The method detection limits of PAHs for water, SPMD, and fish samples were 0.9 to 6.5 ng/L, 2.1 to 14.2 ng/g (wet wt), and 0.4 to 1.9 ng/g (wet wt), respectively.

Some PAHs with very high log octanol/water partition coefficient (K_{ow}) values, such as indeno[1,2,3-*cd*]pyrene, dibenz[*ah*]anthracene, and benzo[*ghi*]perylene, were not detected in water samples but were detected in all exposed fish and SPMD samples. Therefore, they were excluded from the calculation of uptake rate constants. The PAH and OCP concentrations were reported as ng/g SPMD and ng/g wet-weight fish. We did not lipid-normalize SPMD or fish concentration data, because it is inappropriate to do so when some analytes still remain in the linear or curvilinear uptake phases during an exposure [15]. Only very small amounts of a few low-molecular-weight PAHs with log $K_{ow} < 4.5$ (total PAHs, ~14 ng/g wet wt) were detected in reference fish samples and other

laboratory blank samples. No detectable concentrations of OCPs were found in these samples.

RESULTS AND DISCUSSION

Data overview and modeling

Data in Table 1 delineate the similarities and differences in the concentrations of the 16 PAHs and 13 OCPs measured in fish, SPMDs, and surface-water samples. After 32 d, total concentrations of PAHs in fish (wet wt) and in whole SPMDs (membrane plus lipid) averaged 49.5 and 716.9 ng/g, respectively (the role of metabolism in PAH concentrations found in fish tissues is discussed later). The total concentrations of OCPs in the fish and SPMDs at 32 d were 13.6 and 62.3 ng/g, respectively.

To predict chemical concentration in water from its concentration in SPMD or fish, the uptake (k_u) and/or elimination rate constants (k_e) and the SPMD/water partition coefficient (K_{SPMD}) or the bioconcentration factor are required. One-com-

partment models proposed by Huckins et al. [14,17] can be used to derive most of these parameters. For example, the following model describes the first-order exponential uptake of HOCs by SPMDs and BMOs:

$$C_{sm} = (k_u/k_e)C_w[1 - \exp(-k_e t)] \quad \text{and} \quad (1)$$

$$k_u/k_e = C_{sm-ss}/C_w = K_{sw} \quad (2)$$

where C_{sm} is the concentration of the analyte in the whole sampling matrix (ng/g), C_w is the concentration in ambient water (ng/L), k_u is the linear uptake rate constant (L/d·g), k_e is the elimination rate constant (1/d), t is time (d), C_{sm-ss} is the steady-state concentration of the analyte in a sampling matrix (ng/g), and K_{sw} (i.e., bioconcentration factor [K_{SPMD}]) is the steady-state partition coefficient between the sampling matrix and the water sampled. Equation 1 shows that the concentration in the sampling matrix gradually increases with time until equilibrium is attained. When $k_e t \ll 1$, the group between square brackets in Equation 1 is approximately equal to $k_e t$, and then Equation 1 reduces to a linear model:

$$C_{sm} = k_u C_w t \quad (3)$$

When $k_e t \gg 1$, Equation 1 reduces to an equilibrium model (identical to Eqn. 2).

Huckins et al. [15] also have developed an equation that enables investigators to estimate SPMD K_{sw} values directly from K_{OW} values:

$$\log K_{sw} = -0.1618(\log K_{OW})^2 + 2.321 \log K_{OW} + a_0 \quad (4)$$

where a_0 is -2.61 for nonpolar compounds. Booi et al. [18] has found that K_{sw} is independent of temperature within the range of 2 to 30°C. In the low to moderate K_{OW} range (i.e., $\log K_{OW} < 5.3$), contaminants generally approach equilibrium or uptake is in the curvilinear region in both matrices in the present study. Also, biofouling impedance of uptake is lower for these compounds [15]. Therefore, Equation 1 was used to derive k_u and k_e values for chemicals with $\log K_{OW} < 5.3$. To estimate parameters in the model equation, the Marquardt-Levenberg nonlinear least-squares algorithm in SPSS 10.0 software for Windows® (SPSS, Chicago, IL, USA) was used. For HOCs still in the linear uptake phase (those with $\log K_{OW} > 5.3$), the k_u values were calculated by fitting the experimental data to Equation 3 by linear least-squares regression in SPSS. Equation 4 was used to derive K_{sw} values, and then k_e values were derived from k_u/K_{sw} .

Because of membrane permeability limitations (as a result of the size of transient cavities of low-density polyethylene and gill membrane), SPMDs and most finfish accumulate only dissolved chemicals and exclude chemicals associated with sorptive organic carbon. Several investigators have suggested that the presence of dissolved organic carbon (DOC) in exposure water would decrease the dissolved concentration, resulting in lowering the apparent rate constants of high- K_{OW} compounds [19,20]. Furthermore, previous studies have shown that the solid-phase extraction method used for water samples in the present study failed to distinguish between truly dissolved and DOC-associated chemicals [21,22]. Therefore, without correcting for DOC attenuation of high- K_{OW} compounds, their true uptake rate constants likely are underestimated.

Hence, to examine the potential attenuating effects of DOC on SPMD and crucian carp apparent uptake rate constants, an equation used by Meadows et al. [19] was adopted:

Table 2. Exchange coefficients (k_u and k_e) for semipermeable membrane devices (SPMDs) and crucian carp as determined from surface-water exposure of Meiliang Bay, Taihu Lake, China

Compounds ^a	SPMDs ^b			Crucian carp ^b		
	k_u^c (L/g·d)	CV (%)	k_e (1/d)	k_u^c (L/g·d)	CV (%)	k_e (1/d)
PAHs						
Naphthalene	0.21	10	0.16	0.047	21	0.27
Acenaphthylene	0.24	17	0.13	0.049	25	0.21
Acenaphthene	0.44	16	0.11	0.060	37	0.24
Fluorene	0.35	21	0.08	0.077	20	0.21
Phenanthrene	0.69	8	0.09	0.098	36	0.16
Anthracene	0.43	22	0.06	0.093	40	0.21
Fluoranthene	0.88	25	0.06	0.100	23	0.15
Pyrene	1.02	14	0.07	0.090	31	0.13
Benz[a]anthracene	0.71	14	0.002	0.085	12	0.04
Chrysene	0.64	7	0.04	0.093	26	0.10
Benzo[b]fluoranthene	0.60	11	0.002	0.081	44	0.07
Benzo[k]fluoranthene	0.49	23	0.001	0.060	25	0.03
Benzo[a]pyrene	0.60	22	0.001	0.065	39	0.03
OCPs						
α-Endosulfan	0.16	11	0.16	0.017	32	0.10
γ-HCH	0.05	15	0.14	0.013	25	0.09
β-HCH	0.11	18	0.20	0.032	37	0.16
α-HCH	0.20	20	0.16	0.015	21	0.16
δ-HCH	0.29	9	0.15	0.026	25	0.14
Heptachlor epoxide	0.57	14	0.10	0.068	34	0.04
Heptachlor	0.98	15	0.07	0.396	16	0.12
Hexachlorobenzene	0.96	8	0.004	0.406	28	0.07
4,4'-DDD	1.01	14	0.004	0.642	16	0.08
4,4'-DDE	0.95	11	0.003	0.500	31	0.04
cis-Chlordane	0.33	12	0.001	0.151	24	0.07
trans-Chlordane	1.02	16	0.002	0.306	14	0.02
4,4'-DDT	0.44	24	0.001	0.098	28	0.07

^a PAH = polycyclic aromatic hydrocarbon; OCP = organochlorine pesticides; HCH = hexachlorocyclohexane; DDD = dichlorodiphenylchloroethane; DDE = dichlorodiphenylethane.

^b Mean values ($n = 3$ for SPMD and $n = 5$ for crucian carp); CV = coefficient of variation.

^c Corrected for 5 mg/L of dissolved organic carbon and the assumption $K_{DOC} = 0.11K_{OW}$.

$$C_{wd} = m_{a(tot)}/(V_w + V_{DOC}K_{DOC}) \quad (5)$$

where C_{wd} is the concentration of dissolved HOCs in the water, $m_{a(tot)}$ is the total mass of analyte, V_w is the volume of water, and V_{DOC} is the volume of DOC (assumes a DOC density of 1.0) in V_w . The result of the TOC analysis shows that lake water of the study site contains approximately 5 mg/L of DOC. In the present work, we used the relationship proposed by Burkhard [23] to derive the K_{DOC} of analyte from its K_{OW} . The water concentration (whole concentration) as determined by the solid-phase extraction method and the estimated dissolved concentration for target compounds are given in Table 1. For compounds with $\log K_{OW} \geq 6$, the ratios of whole concentration to the corresponding dissolved concentration are near two (Table 1). This observation further indicates that the attenuation of dissolved-phase concentration by DOC in the studied water had a significant effect on the apparent uptake rate constants of SPMDs and crucian carp for high- K_{OW} contaminants ($\log K_{OW} \geq 6$).

SPMD and fish uptake and elimination rate constants

Values for k_u adjusted for DOC sorption are given in Table 2. It is observed that SPMD rate constants are less variable for a specific compound than for crucian carp. For example, the coefficients of variation of k_u values are less than 45% for

crucian carp and less than 25% for SPMDs. This results, in part, from the reproducible, standardized design of SPMDs. Moreover, residue accumulation in individual fish is less predictable because of differences in behavior and physiological status. Although previous field studies [2,8,24] have shown that SPMDs accumulate higher concentrations of HOCs than aquatic organisms (on a whole-body basis), the reported differences in concentrations do not necessarily reveal differences in sampling rates, because it was not clear whether the organisms were at steady-state by the end of exposure. In the work of Meadows et al. [19], in which uptake remained in the linear phase, k_u values of PCBs in SPMDs were one- to twofold greater than those of brown trout. In another study [25], the uptake rates of five OCPs by SPMDs were 1.0- to 2.5-fold those by rainbow trout. In the present study, uptake rate constants for PAHs and OCPs averaged seven- and fivefold higher, respectively, for SPMDs than for crucian carp. Thus, our data further support previous findings that SPMD uptake rates of HOCs generally are greater than those observed for fish. Although Booij et al. [26] has proposed that contaminant transport rates via the SPMD–water boundary layer and via the boundary layer associated with aquatic organism gill ventilation are of similar magnitude, the difference between SPMD and fish uptake rate constants likely was caused by the different exchange fluxes of contaminants across the SPMD membrane and gill membrane. Even in the case of OCPs, however, differences in our SPMD and fish uptake rate constants are a little larger than those observed in previous studies. The inconsistencies may be attributed, in part, to the interspecies variability of BMOs, because some investigators have stated that certain behavioral, physiological, and anatomical differences across BMO species also affect the bioaccumulation of HOCs [5,24,27].

Our SPMD k_u values for OCPs and PAHs are consistent (within approximately one- to twofold) with the values determined in other studies [14,25,28,29]. The SPMD and crucian carp data given in Table 2 show a consistent trend of k_u values increasing with $\log K_{OW}$ values, reaching a maximum near a $\log K_{OW}$ of six and then decreasing at higher $\log K_{OW}$ values. Because membrane/water partition coefficients generally rise with triolein/water partition coefficients [1], uptake rate constants of HOCs are expected to be related to their lipophilicity for compounds under membrane control of uptake. For HOCs with increasingly high K_{OW} values, membrane resistance falls until the rate-limiting step switches to aqueous boundary layer control. Under relatively quiescent conditions, this switch generally occurs at a $\log K_{OW}$ of approximately 4.5 [14]. Furthermore, uptake rate constants of compounds with $\log K_{OW}$ values of greater than six are expected to fall slowly because of slight decreases in boundary layer diffusion coefficients. The phenomenon of a reduction in the SPMD and fish uptake rates at $\log K_{OW} \geq 6$ has been noted in previous studies [19,20,30]. This reduction in uptake rate constants (primarily for high- K_{OW} compounds) may be related to impedance (because of biofouling [SPMDs]) and permeability limitations (because of the observation that cross-sectional diameters of some analytes approach or exceed the theoretical pore diameters of low-density polyethylene and biomembranes [i.e., 10 and 9.8 Å, respectively]) [1]. In most aquatic systems, biofilms are not well established on SPMD membranes until about one or two weeks of exposure, and for a given thickness of biofilm, impedance to mass transfer is greater for those compounds with high K_{OW} values. These observations are consistent with

Fig. 1. Uptake of benz[a]anthracene and *cis*-chlordane by semipermeable membrane devices (SPMDs) during 32-d exposure. Concentrations are based on the total weight of the SPMD. Error bars represent standard deviations for SPMDs ($n = 3$).

the shapes of plots shown in Figure 1. Although no biofouling was observed on the outer surfaces of exposed SPMD membranes, the apparent change in slope of the uptake curve of benz[a]anthracene and *cis*-chlordane at 8 or 16 d (Fig. 1) suggests that biofouling impedance reduced sampling rates. In addition, a reduction in uptake rate constants in fish can occur because of growth dilution but is unlikely in the present study, because adult fish were used and were not fed during the exposure.

Although SPMD k_u values generally are larger than those of crucian carp (Table 2), the apparent trends of the uptake rate constants of PAHs and OCPs by SPMDs and by crucian carp are similar. The results of linear-regression analysis indicate that the uptake rate constants of SPMDs and fish are correlated for PAHs ($r^2 = 0.55$, $p = 0.004$, $n = 13$) and well correlated for OCPs ($r^2 = 0.81$, $p < 0.001$, $n = 13$) (Fig. 2). A significant difference, however, is observed in the correlation coefficients for PAH and OCP uptake rate constants. The reason for the relatively poor correlation of SPMD and fish k_u values of PAHs compared with k_u values of OCPs is likely the result of PAH metabolism in fish. All fish have microsomal cytochrome P450 enzymes, which enable the biotransformation of PAHs [31]. The close similarities between SPMDs and fish uptake rate constants for contaminants over a large range of K_{OW} values suggest that in this case, SPMDs mimic the process of fish bioconcentration, especially for unmetabolized compounds.

The SPMD and fish k_e values both decreased as hydrophobicity increased (Table 2), which indicates that the kinetics of residue exchange followed a hydrophobicity model [32]. Nevertheless, the fish k_e values are much larger than those of SPMDs, resulting in much shorter half-lives of test compounds. Most of the fish k_e values for the 16 PAHs determined herein agree within approximately one- to fourfold with oyster data published by Huckins et al. [17] and Bender et al. [33]. The divergence of some values is likely because of the significant physiological and behavioral differences between fish and bivalves.

Fig. 2. Relationship between semipermeable membrane device (SPMD) uptake rate constants ($k_{u(\text{SPMD})}$) and crucian carp uptake rate constants ($k_{u(\text{fish})}$) for test polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs).

Comparison of the concentration factors in SPMDs and crucian carp

The PAH concentration factors (CFs) in crucian carp and SPMDs were derived for our 32-d samples and compared to CFs of PAHs in oysters and SPMDs at 20 d [17]. Values of SPMD and crucian carp PAH CFs are given across the wide range of $\log K_{ow}$ values (i.e., 3.45–6.35). The CF values in Table 1 were derived by dividing concentrations of analytes in crucian carp and SPMDs by the dissolved water concentrations rather than by the total concentrations. Our SPMD CF data agree to within 0.4 log units with the SPMD CF data for PAHs reported by Huckins et al. [17]. With the exception of naphthalene, however, our crucian carp PAH CFs are as much as one log unit less than oyster CFs reported by Huckins et al. [17]. A plausible explanation for the divergence of crucian carp and oyster CFs is that cytochrome P450 enzyme levels in fish are much higher than those in bivalves. Thus, PAH

metabolism by crucian carp likely is a very significant factor in the divergence of crucian carp and oyster CFs. Furthermore, PAH CFs generally were 0.9 to 1.4 log units lower in crucian carp than in SPMDs (Table 1). A number of studies [2,8,19] have shown that SPMDs accumulate higher concentrations of hydrophobic pollutants than most aquatic organisms (based on whole-body residues) when deployed side by side, especially for low- K_{ow} compounds. Complex active biological processes of test organisms likely are responsible for some of this divergence.

Although equilibrium was not attained for most compounds in SPMD and nearly half the compounds in crucian carp during our 32-d exposure period, correlations between 32-d SPMD log CF and $\log K_{ow}$ ($r = 0.86$, $p < 0.001$, $n = 26$) and 32-d crucian carp log CF and $\log K_{ow}$ ($r = 0.75$, $p < 0.001$, $n = 26$) can be observed in Figure 3. This figure indicates that SPMDs and fish concentrate PAHs and OCPs in a similar manner and that the accumulation of individual PAHs and OCPs can be predicted by its $\log K_{ow}$. These findings further support the applicability of the biomimetic nature of SPMDs and their potential as surrogates for biomonitoring work.

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Fig. 3. Relationship between $\log K_{ow}$ values and the 32-d concentration factors (CFs) of semipermeable membrane device (SPMD) and crucian carp for test chemicals.

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