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Estimation of Uptake Rate Constants for PCB Congeners Accumulated by Semipermeable Membrane Devices and Brown Trout (*Salmo trutta*)

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The triolein-filled semipermeable membrane device (SPMD) is a simple and effective method of assessing the presence of waterborne hydrophobic chemicals. Uptake rate constants for individual chemicals are needed to accurately relate the amounts of chemicals accumulated by the SPMD to dissolved water concentrations. Brown trout and SPMDs were exposed to PCB-contaminated groundwater in a spring for 28 days to calculate and compare uptake rates of specific PCB congeners by the two matrixes. Total PCB congener concentrations in water samples from the spring were assessed and corrected for estimated total organic carbon (TOC) sorption to estimate total dissolved concentrations. Whole and dissolved concentrations averaged 4.9 and 3.7 μg/L, respectively, during the exposure. Total concentrations of PCBs in fish rose from 0.06 to 118.3 μg/g during the 28-day exposure, while concentrations in the SPMD rose from 0.03 to 203.4 μg/g. Uptake rate constants (k_1) estimated for SPMDs and brown trout were very similar, with k_1 values for SPMDs ranging from one to two times those of the fish. The pattern of congener uptake by the fish and SPMDs was also similar. The rates of uptake generally increased or decreased with increasing K_{OW}, depending on the assumption of presence or absence of TOC.

Introduction

The semipermeable membrane device (SPMD) is a passive sampler that mimics the bioconcentration of organic pollutants from water by aquatic organisms (*1*). The device enables investigators to detect extremely low amounts of organic contaminants dissolved in aquatic environments (*2*−*4*). A significant difficulty encountered with the use of this device is the lack of calibration data to accurately relate amounts of accumulated contaminants to the concentrations of those compounds in the environment.

The amount of a waterborne chemical accumulated by the SPMD is affected by environmental variables such as temperature, total organic carbon (TOC) content of the water, effective boundary layer thickness, and biofouling (*5*−*7*). These variables appear to affect compounds of similar physicochemical characteristics proportionally, and therefore their effects on SPMD sampling should be predictable. A method to estimate correction factors for these sampling variables has been developed (*8*). Huckins et al. (*4*) have shown that individual compounds are accumulated at different rates by the SPMD even under identical exposure conditions.

The capacity of an SPMD to accumulate a dissolved organic contaminant is generally related to the contaminant's octanol/water coefficient (K_{ow}) (*1*). The K_{ow} values of organic contaminants span several orders of magnitude. This parameter or the similar triolein/water partition coefficient (*9*) along with the physicochemical characteristics of the SPMD membrane and the contaminant molecule and environmental conditions combine to affect the chemical's rate of accumulation. The linear uptake of dissolved lipophilic chemicals has been described (*4*) by the following relationship:

$$C_{S(T)} = \frac{C_{Wd} K_{MW} k_0 A t}{V_{S(T)}} \quad (1)$$

where $C_{S(T)}$ is analyte concentration in SPMD triolein, C_{Wd} is the analyte concentration dissolved in the water, K_{MW} is the membrane−water partition coefficient, k_0 is the overall mass transfer coefficient (aqueous diffusional layer, periphyton, and membrane), A is the membrane surface area, t is exposure time, and $V_{S(T)}$ is the volume of triolein in the SPMD (*4*). The group $K_{MW}k_0A$ can be viewed as the SPMD uptake rate or sampling rate, $R_{S(T)}$, in units of liters per day for an SPMD in this configuration. $R_{S(T)}$ represents the volume of water that is cleared of chemical by the device per unit time. Then, rearranging eq 1

$$C_{Wd} = \frac{C_{S(T)} V_{S(T)}}{R_{S(T)} t} \quad (2)$$

or

$$R_{S(T)} = \frac{C_{S(T)} V_{S(T)}}{C_{Wd} t} \quad (3)$$

For convenience, it is assumed that all the chemical recovered by the SPMD is in the triolein. In reality, $R_{S(T)}$ includes the contribution of both the triolein and membrane phases.

The $R_{S(T)}$ value must be measured for individual compounds under relatively constant exposure conditions. With $R_{S(T)}$ values, it is possible to accurately relate the amounts of individual compounds accumulated by an SPMD to the concentrations of these chemicals in similar environments. Uptake rates by SPMDs have been measured under laboratory conditions by the use of flow-through diluters (*10*). This approach is costly in terms of equipment and human resources and generates a significant amount of contaminated effluent (*4*).

Little SPMD uptake rate data are available for polychlorinated biphenyls (PCBs). The 209 PCB congeners vary tremendously in toxicity, rendering congener-specific uptake rate information highly pertinent to toxicity assessments. The opportunity to obtain data to estimate uptake rate constants for PCB congeners under field conditions was afforded by a unique field site. The Commonwealth of Pennsylvania is currently monitoring several sites on or around natural gas pipeline compressor stations that have

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become contaminated by PCBs. PCBs have been found in groundwater, surface waters, stream sediments, and fishes. At one site, groundwater percolates through PCB-contaminated soil and is discharged from a nearby spring. The spring maintains a fairly constant discharge of waterborne PCBs at or near their water solubility levels, and the temperature of the spring water remains relatively constant. The spring is enclosed in a spring house, which provided restricted access. Therefore, the field site provided excellent conditions for exposure of the brown trout and SPMDs to the contaminated groundwater. The objectives of this paper are to utilize the data obtained in the 28-day exposure to estimate sampling rate constants for selected PCB congeners by SPMDs and to compare the rates of uptake of these congeners by brown trout.

Experimental Section

Materials. All solvents used in the study were Fisher Optima (universal) grade or the equivalent. Polychlorinated biphenyl mixtures for use in spike recovery studies and residue analysis were obtained from the U.S. EPA Repository for Toxic and Hazardous Materials, Research Triangle Park, NC. The individual PCB congeners used as recovery standards were obtained from Ultra Scientific, North Kingstown, RI. The SPMDs were constructed from low-density layflat polyethylene (PE) tubing (2.5 cm wide; ≃86 μm wall thickness) from Brentwood Plastics, Inc., St. Louis, MO. Each SPMD was 2.5 cm wide, 91 cm long, contained 1 mL (0.91 g) of triolein, and weighed 4.55 g. The brown trout averaged 40 g in weight and were obtained from the Oswayo Fish Culture Station, Potter County, Pennsylvania.

Sample Collection. The SPMDs were secured by L-shaped hooks to a rectangular rack (110 × 56 × 2.5 cm) constructed of wood and metal. Eighteen SPMDs were mounted on the rack, which was deployed in the spring. A cage (0.8 × 0.4 × 0.4 m) constructed of a wood frame and plastic mesh confined the fish during the exposure. The fish, SPMDs, and water were sampled at 0, 7, 14, and 28 days. Triplicate 4-L water samples, triplicate trout samples (2−3 trout per sample), and triplicate SPMD samples (two SPMDs per sample) were removed at each time point. Water samples and the SPMDs were refrigerated and shipped immediately after collection. The trout were frozen after sampling and shipped after completion of the last (28-day) exposure period. Water temperatures ranged from 10.5 to 12.6 °C and averaged 11.8 °C. Flow, which was measured at day 0, 7, 14, and 28, averaged 11 630 L/day. At that flow rate, the refresh rate of the spring pool was 2.9 h.

Sample Preparation. The water samples were collected in 4-L amber glass bottles with Teflon-lined caps, leaving no headspace. The samples were not preserved or stabilized with an organic solvent but were extracted immediately upon receipt by liquid/liquid partitioning with methylene chloride. A matrix blank (4 L of distilled water), a matrix spike (4 L of distilled water spiked with 20 μg of mixed Aroclors 1242, 1248, 1254, and 1260; 1:1:1:1), and a 5-g aliquant of our laboratory's standard positive control material, common carp (*Cyprinus carpio*) from Saginaw Bay, MI, were processed with the group of samples. PCB congeners 030 (2,4,6-trichlorobiphenyl) and 204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl) were used as procedural reference standards (PRS). The exposed SPMDs were first cleaned by physical scrubbing to remove periphyton and particulate matter. Before processing, one of each pair was opened and spiked with the PRS. Two blank sets of SPMDs, prepared on the day dialysis was begun, served as a matrix blank and a matrix spike. The matrix spike sample was fortified with 20 μg of mixed Aroclors (1242, 1248, 1254, and 1260; 1:1:1:1). Each SPMD pair was dialyzed in 1 L of hexane for 48 h. An aliquant of the Saginaw Bay carp was extracted and added to the SPMD sample set after dialysis and solvent reduction. The exposed fish were thawed at room temperature and ground. Aliquants for analysis were removed and dehydrated with four times their weight of anhydrous sodium sulfate. One of the samples was analyzed in triplicate. A matrix blank and spike (spiked with 20 μg of mixed Aroclors) made from clean bluegill (*Lepomis macrochirus*) tissue and a positive control sample of Saginaw Bay carp were processed with the sample group as quality control. The samples were spiked with PRS and extracted with methylene chloride. Percent lipid analysis was performed on the extracts.

All sample extracts were cleaned by reactive adsorbent cleanup (*11*) and high-performance gel permeation chromatography (HPGPC) prior to gas chromatography.

Instrumental Analysis. Congener-specific PCB analysis for 101 peaks was performed on a Hewlett-Packard model 5890 series II gas chromatograph equipped with a ^{63}Ni electron capture detector as described by Feltz et al. (*12*). Cool on-column injections (1 μL) of purified sample extracts were made on a 60 m × 0.25 mm × 0.25 μm DB-5 capillary column with a 2-m deactivated retention gap. The carrier gas was hydrogen (25 psig). The temperature program was as follows: from the initial temperature of 40 °C, the program immediately ramped 10 °C/min to 120 °C, then 2 °C/min to 260 °C with a 2 min hold, and finally ramped 10 °C/min to 320 °C and held for 24 min. Capillary GC/ECD data were collected, archived in digital form, and processed using a PE-Nelson chromatography data system with Turbochrom software. Quantitation was by internal standard method. Total PCB concentrations are expressed as the sum of the individual congener concentrations.

Results and Discussion

Measured water concentrations of total PCBs dropped after the beginning of the exposure. This appeared to be due to natural hydrologically driven (flow-dependent) variation in PCB dissolution and not depletion of dissolved residues by the SPMDs, fish, and cage materials. It is unlikely that the sampling matrixes significantly altered water concentrations, considering the comparatively high flow rate of the spring (8 L/min) as compared to the calculated uptake rate constants of the sampling matrixes. Concentrations of PCBs during the exposure varied between 3.4 ± 0.5 and 6.6 ± 0.6 μg/L total PCBs and averaged 4.9 ± 1.7 μg/L. In 1993, PCB concentrations were measured daily at this spring over a 2-week period, and concentrations ranged from 3.11 to 4.75 μg/L. However, the apparent PCB concentration 2 weeks later was 8.5 μg/L. The average water concentration during the exposure was compared to the historical PCB concentration data, and no statistical difference was found at a $p <$ 0.05 level of significance. Therefore, water concentrations were considered relatively constant, and average values of the individual congeners were used in calculations involving water concentrations.

Whole water samples for this study were extracted by liquid/liquid partitioning. Therefore, the measured concentrations of PCBs in the water reflect both dissolved and organic carbon-associated compounds. Because of physical reasons, SPMDs accumulate only dissolved chemicals (*1*, *4*). The fish in this study were not fed during the exposure, so their primary source of contaminants was respiratory uptake of dissolved chemicals. Since the magnitude of the dissolved fraction of nonpolar aqueous contaminants is related to the organic carbon content of the water, it is important to account for this variable in determining the rates of accumulation of these chemicals by SPMDs and fish and in any extrapolation of accumulated chemicals in these matrixes to water concentrations (*13*).

The influence of organic carbon content of water on the bioavailability of aqueous contaminants is yet to be clearly

and quantitatively defined. The sorption theory proposed by Karickhoff et al. (*14*−*15*) describes the general thermodynamic partitioning process that occurs between the water and the organic carbon content of particulates. The partitioning of a compound between these compartments is represented by the compound's organic carbon sorption coefficient, K_{OC}. Theory suggests that the relationship between K_{OC} and K_{OW} should be dependent on compound class as well as organic carbon quality, but for orders of magnitude accuracy, the relationship, K_{OC}/K_{OW}, can be assumed to be close to unity (*16*). Therefore, for our calculations, we have assumed that K_{OC} is equal to K_{OW} and that, for the purpose of estimating analyte partitioning between the water and the TOC, the TOC content of the water did not vary. Experimentally determined K_{OW} values are not available for all PCB congeners. However, a number of methods of estimating these constants have been proposed (*17*−*20*). In this work, we used the values generated by Hawker and Connell (*20*), which were calculated based on the relationship between total molecular surface area and log K_{OW} and confirmed by comparison with a set of K_{OW} values obtained from a generator column determination.

Samples of the contaminated spring water were analyzed for TOC and were found to contain less than our method detection limit (MDL) of 1.0 mg/L. However, the presence of nondetected concentrations (<1.0 mg/L) of dissolved or colloidal carbon is likely and may have significant effects on the concentrations of truly dissolved high K_{OW} PCBs. Several investigators have suggested that small particulates or colloids (≤0.45 μm) along with truly dissolved organic molecules should be viewed as a "third phase" in the environment (*21*, *24*) which, due to its sorption of hydrophobic chemicals, enhances the apparent solubility of the chemicals in water. The undetected presence of this phase in the uptake model of SPMDs or biota would therefore lower the apparent rate of accumulation of affected compounds (*21*−*24*). To test this hypothesis, the TOC was assumed to be half the MDL or 0.5 mg/L. According to Spacie et al. (*25*), the concentration of a hydrophobic chemical in water that is dissolved is related to the TOC content of the water by the following equation:

$$C_{Wd} = \frac{m_{a(tot)}}{m_W + m_{OC}K_{OC}} \tag{4}$$

where $m_{a(tot)}$ is the total mass of analyte, m_W is the mass of water, and m_{OC} is the mass of organic carbon in m_W. Applying this equation to the individual congeners, the total dissolved water concentrations of the PCBs we quantified averaged 3.7 μg/L, assuming a TOC of 0.5 mg/L (Table 1). The corresponding measured (whole water) concentration was 4.9 μg/L. Given the range of log K_{OW} values (5.0−7.7, Table 1) for the PCBs detected, if m_{OC} is postulated to range from 0.05 to 1.0 mg/L, the fractional amount of dissolved PCB (C_{Wd}/C_W) would range between 0.99 and 0.3 (0.05 mg/L, m_{OC}) and between 0.99−0.02 (1.0 mg/L, m_{OC}).

Total organic carbon content of the water is especially critical in determining uptake kinetics of high K_{OW} compounds by SPMDs or biota because of its effect on the dissolved, or bioavailable, portion of waterborne contaminants (e.g., dissolved concentrations of PCBs with log K_{OW} greater than 7 are reduced more than 80% when correcting for 0.5 mg/L TOC). This observation is illustrated by the increasing differences in TOC-corrected vs uncorrected k_1 (uptake) values in Table 1. The aqueous TOC concentrations (if present) were lower than our method detection limit, therefore k_1 values corrected for implicit TOC concentrations must be viewed as rough approximations. However, this work illustrates the range of potential PCB k_1 values for SPMDs and fish that are possible when correcting for attenuation of aqueous residues by TOC (0.5 mg/L) and when assuming no correction is needed. Because K_{OC} values could be expected to vary considerably depending on organic carbon quality, k_1 values would be best determined in water free of organic carbon. The water used in this study had lower TOC than observed in most surface waters.

As stated earlier, eq 3 is based on the assumption that all the chemical accumulated by the SPMD is in the triolein. However, previous studies have indicated that the polyethylene portion of the SPMD is itself a significant reservoir, containing up to 50% of the accumulated contaminants (*10*). The membrane is a functional constituent in the sampling process rather than simply a container for the triolein. Therefore, the linear uptake rate described by eq 3 might more clearly be expressed in units of liter per day per SPMD. The residue kinetics and thermodynamics in both the membrane and lipid phases directly affect the equilibration period, capacity to accumulate contaminants, and the k_1 and k_2 (depuration) values for the device. A standard comercially available configuration of SPMD was used in this work. This sampler has a total mass of 4.55 g, which contains 0.91 g (1 mL) of triolein and represents a 4:1 polyethylene:triolein (PE:T) ratio (*1*).

PCB concentrations in the SPMDs (C_S) were normalized to the sampler weight by substituting the mass of the sampler (m_S) for V_T in eq 3:

$$R_S = \frac{C_S m_S}{C_{Wd} t} \tag{5}$$

Equation 5 should apply to any size or portion of SPMD, assuming the layflat tubing used is the same and the 4:1 PE:T ratio is maintained.

The *sampling rate constant* of the sampler ($k_{1(S)}$) is related to R_S by the equation (*17*):

$$k_{1(S)} = \frac{R_S}{m_S} = \frac{C_S}{C_{Wd} t} \tag{6}$$

The SPMD sampling rate constants are thus expressed in terms of liters per day per gram, allowing direct comparisons to k_1 values for fish or other organisms. The $k_{1(S)}$ for SPMDs constructed in the 4:1 PE:T ratio are given in Table 1.

A variety of k_1 values have been calculated for chemicals accumulated by fish ($k_{1(F)}$). The values for the same chemical vary because of differences in species, sex, life stage, health, lipid composition, and water temperature (*9*, *26*−*31*). While it is difficult to quantitatively compare values for $k_{1(F)}$ and $k_{1(S)}$, the relative uptake rates of congeners not metabolized by fish should be proportional if the SPMD mimics the process of fish bioconcentration. Values for k_1 for SPMDs and brown trout are given in Table 1. The $k_{1(F)}$ values were calculated using eq 6, substituting the concentrations of the analytes per gram of fish tissue for C_S in the equation. Rate constant calculations were performed for each replicate of each time period for both fish and SPMDs. The rate constants in Table 1 are averages of the nine values for each matrix. The k_1 values vs log K_{OW} are plotted in Figure 1, panels a and b. Uptake rates uncorrected and corrected for implicit TOC (0.5 mg/L) are plotted for each matrix. Rates remained relatively constant throughout the exposure and the trends of contaminant uptake by fish and SPMDs are similar. The plots also illustrate that the *apparently* lower uptake rate of the more hydrophobic compounds is actually higher if TOC sorption is considered. Figure 1c shows that the PCB uptake rates of SPMDs and fish (corrected for TOC sorption) are correlated ($r^2 = 0.89$), suggesting that the variance in TOC-correlated data in Figure 1a,b is due to errors associated with the $K_{OC} \simeq K_{OW}$ assumption. This close similarity between SPMDs and fish uptake rates over a large range of K_{OW} values is different than that reported in similar surface water

TABLE 1. PCB Uptake Rate Constants for SPMDs and Brown Trout Estimated from Field Exposure to Contaminated Spring Water[a]

			water concn		SPMD $k_{1(S)}$		trout $k_{1(F)}$	
IUPAC no.	structure	log K_{OW}	whole (ng/L)	dissolved (ng/L)[b]	uncorrected for TOC (L/g·d)[c]	corrected for TOC (L/g·d)[b,c]	uncorrected for TOC (L/g·d)[b]	corrected for TOC (L/g·d)[b,c]
006	2,3′-	5.06	0.1	0.1	2.9 (0.8)	3.0 (1.6)	1.5 (0.4)	1.6 (0.4)
018	2,2′,5-	5.24	254.3	234.0	2.1 (0.5)	2.2 (0.9)	1.1 (0.2)	1.2 (0.0)
019	2,2′,6-	5.02	126.4	120.1	1.2 (0.2)	1.3 (0.2)	0.7 (0.1)	0.7 (0.0)
022	2,3,4′-	5.58	86.9	73.0	1.3 (0.2)	1.6 (0.5)	0.9 (0.1)	1.0 (0.0)
025	2,3′,4-	5.67	7.7	6.2	1.3 (0.2)	1.6 (0.3)	0.7 (0.2)	0.8 (0.0)
026	2,3′,5-	5.66	24.1	19.6	1.3 (0.2)	1.6 (0.3)	0.7 (0.2)	0.8 (0.0)
028	2,4,4′-	5.67	128.6	104.3	1.9 (0.4)	2.3 (1.3)	1.0 (0.2)	1.3 (0.0)
031	2,4,5′-	5.67	47.4	38.4	1.6 (0.7)	2.0 (1.3)	0.8 (0.2)	1.0 (0.0)
040	2,2′,3,3′-	5.66	93.5	76.1	1.5 (0.4)	1.9 (0.7)	0.7 (0.1)	0.9 (0.0)
041	2,2′,3,4-	5.69	210.3	169.0	1.4 (0.5)	1.7 (1.3)	0.6 (0.1)	0.8 (0.0)
042	2,2′,3,4′-	5.76	322.3	250.3	1.4 (0.3)	1.8 (0.6)	0.7 (0.1)	1.0 (0.0)
043	2,2′,3,5-	5.75	11.9	9.3	1.4 (0.2)	1.8 (0.7)	na[d]	na
044	2,2′,3,5′-	5.75	415.8	324.5	1.7 (0.4)	2.2 (0.8)	0.9 (0.1)	1.2 (0.0)
045	2,2′,3,6-	5.53	156.0	133.4	1.8 (0.4)	2.1 (0.9)	0.9 (0.1)	1.1 (0.0)
046	2,2′,3,6′-	5.53	75.2	64.3	1.0 (0.1)	1.2 (0.2)	0.4 (0.1)	0.5 (0.0)
047	2,2′,4,4′-	5.85	126.7	93.6	1.7 (0.5)	2.3 (0.8)	0.9 (0.3)	1.2 (0.0)
048	2,2′,4,5-	5.78	83.4	64.1	0.8 (0.0)	1.1 (0.2)	0.9 (2.5)	1.1 (0.0)
049	2,2′,4,5′-	5.85	321.5	237.4	1.2 (0.2)	1.6 (0.3)	1.1 (0.1)	1.5 (0.0)
051	2,2′,4,6′-	5.63	38.2	31.5	1.1 (0.2)	1.3 (0.2)	0.5 (0.1)	0.6 (0.0)
052	2,2′,5,5′-	5.84	522.0	387.8	1.4 (0.2)	1.8 (1.7)	1.0 (0.1)	1.4 (0.0)
053	2,2′,5,6′-	5.62	133.7	110.7	1.1 (0.2)	1.4 (0.3)	na	na
063	2,3,4′,5-	6.17	11.2	6.4	1.2 (0.2)	2.1 (0.4)	0.6 (0.2)	1.1 (0.0)
064	2,3,4′,6-	5.95	190.4	131.7	1.7 (0.5)	2.5 (1.1)	0.9 (0.1)	1.4 (0.0)
066	2,3′,4,4′-	6.2	179.5	100.1	1.2 (0.3)	2.2 (0.5)	na	na
067	2,3′,4,5-	6.2	7.5	4.2	1.2 (0.2)	2.1 (0.3)	0.6 (0.2)	1.1 (0.0)
070	2,3′,4′,5-	6.2	130.7	72.9	1.6 (0.4)	2.8 (1.1)	0.9 (0.1)	1.6 (0.0)
074	2,4,4′,5-	6.2	103.9	58.0	1.4 (0.6)	2.5 (2.1)	0.7 (0.2)	1.3 (0.0)
081	3,4,4′,5-	6.36	1.9	0.9	1.1 (0.3)	2.2 (1.1)	na	na
082	2,2′,3,3′,4-	6.2	18.4	10.3	1.0 (0.1)	1.8 (0.3)	0.5 (0.1)	0.9 (0.0)
083	2,2′,3,3′,5-	6.26	6.4	3.4	1.1 (0.1)	2.1 (0.3)	0.5 (0.1)	1.0 (0.0)
084	2,2′,3,3′,6-	6.04	44.3	28.6	1.0 (0.2)	1.6 (0.3)	0.4 (0.1)	0.7 (0.0)
085	2,2′,3,4,4′-	6.3	17.1	8.6	1.1 (0.2)	2.3 (0.6)	na	na
087	2,2′,3,4,5′-	6.29	38.9	19.7	1.2 (0.3)	2.4 (0.6)	0.7 (0.1)	1.3 (0.0)
090	2,2′,3,4′,5-	6.36	4.8	2.2	1.4 (0.2)	3.0 (1.0)	na	na
091	2,2′,3,4′,6-	6.13	25.1	15.0	1.0 (0.1)	1.6 (0.2)	0.5 (0.1)	0.8 (0.0)
092	2,2′,3,5,5′-	6.35	11.9	5.6	1.2 (0.2)	2.5 (0.5)	0.5 (0.1)	1.2 (0.0)
095	2,2′,3,5′,6-	6.13	65.7	39.2	1.4 (0.4)	2.3 (0.9)	na	na
097	2,2′,3′,4,5-	6.29	34.1	17.3	1.0 (0.1)	2.1 (0.3)	0.6 (0.2)	1.1 (0.0)
099	2,2′,4,4′,5-	6.39	35.9	16.1	1.0 (0.2)	2.3 (0.4)	0.5 (0.1)	1.1 (0.0)
101	2,2′,4,5,5′-	6.38	51.4	23.4	1.4 (0.3)	3.0 (0.9)	1.4 (0.3)	3.0 (0.0)
105	2,3,3′,4,4′-	6.65	19.8	6.1	0.9 (0.3)	2.9 (0.8)	0.6 (0.2)	1.9 (0.0)
107	2,3,3′,4′,5-	6.71	2.5	0.7	1.2 (0.2)	4.2 (2.4)	0.6 (0.2)	2.1 (0.0)
110	2,3,3′,4′,6-	6.48	61.8	24.6	1.3 (0.5)	3.3 (1.1)	0.6 (0.2)	1.4 (0.0)
114	2,3,4,4′,5-	6.65	1.6	0.5	1.0 (0.2)	3.2 (0.7)	na	na
118	2,3′,4,4′,5-	6.74	24.8	6.6	1.1 (0.1)	4.2 (0.5)	0.6 (0.1)	2.1 (0.0)
119	2,3′,4,4′,6-	6.58	1.6	0.5	1.0 (0.1)	3.0 (0.7)	0.6 (0.2)	1.7 (0.0)
128	2,2′,3,3′,4,4′-	6.74	1.5	0.4	1.0 (0.2)	3.6 (0.8)	0.5 (0.1)	2.0 (0.0)
129	2,2′,3,3′,4,5-	6.73	0.6	0.2	0.8 (0.1)	2.9 (1.1)	0.4 (0.2)	1.6 (0.1)
130	2,2′,3,4,4′,5-	6.8	0.5	0.1	0.9 (0.2)	3.7 (0.9)	0.5 (0.1)	2.2 (0.1)
134	2,2′,3,3′,5,6-	6.55	0.7	0.2	1.1 (0.1)	3.1 (1.6)	0.7 (0.2)	2.1 (0.1)
136	2,2′,3,3′,6,6′-	6.22	2.0	1.1	1.2 (0.3)	2.2 (0.6)	0.5 (0.2)	1.0 (0.0)
137	2,2′,3,3′,4,5′-	6.83	0.5	0.1	0.8 (0.2)	3.3 (0.8)	0.4 (0.1)	2.0 (0.1)
138	2,2′,3,4,4′,5′-	6.83	7.6	1.8	1.1 (0.1)	4.9 (1.2)	0.5 (0.1)	2.4 (0.0)
141	2,2′,3,4,5,5′-	6.82	1.7	0.4	1.1 (0.3)	4.6 (1.4)	0.5 (0.2)	2.3 (0.0)
146	2,2′,3,4′,5,5′-	6.89	1.0	0.2	1.1 (0.2)	5.3 (1.2)	0.7 (0.2)	3.4 (0.1)
149	2,2′,3,4′,5′,6-	6.67	8.5	2.6	1.3 (0.1)	4.4 (0.8)	0.6 (0.2)	2.1 (0.0)
151	2,2′,3,5,5′,6-	6.64	2.7	0.9	1.2 (0.2)	3.8 (1.3)	0.7 (0.1)	2.1 (0.0)
153	2,2′,4,4′,5,5′-	6.92	3.6	0.7	0.8 (0.2)	4.2 (1.5)	0.7 (0.2)	3.4 (0.0)
156	2,3,3′,4,4′,5-	7.18	0.6	0.1	0.6 (0.2)	5.5 (2.3)	na	na
157	2,3,3′,4,4′,5′-	7.18	0.3	0.04	0.6 (0.1)	4.8 (2.4)	na	na
158	2,3,3′,4,4′,6-	7.02	0.7	0.1	0.8 (0.2)	5.1 (2.1)	0.4 (0.1)	2.6 (0.1)
172	2,2′,3,3′,4,5,5′-	7.33	0.3	0.03	0.3 (0.0)	3.1 (1.2)	0.1 (0.0)	1.7 (0.2)
174	2,2′,3,3′,4,6,6′-	7.11	1.7	0.2	0.7 (0.2)	5.5 (1.7)	0.4 (0.1)	2.7 (0.0)
176	2,2′,3,3′,4′,5,6-	6.76	0.3	0.1	0.5 (0.2)	1.9 (1.0)	0.3 (0.1)	1.3 (0.1)
177	2,2′,3,3′,4′,5,6-	7.08	0.9	0.1	0.7 (0.1)	5.0 (1.6)	0.4 (0.1)	2.7 (0.1)
178	2,2′,3,3′,5,5′,6-	7.14	0.3	0.04	0.7 (0.1)	5.7 (1.4)	0.6 (0.2)	4.4 (0.3)
179	2,2′,3,3′,5,6,6′-	6.73	0.8	0.2	0.5 (0.1)	1.9 (0.7)	0.4 (0.2)	1.6 (0.1)
180	2,2′,3,4,4′,5,5′-	7.36	2.8	0.2	0.6 (0.1)	7.7 (1.7)	0.4 (0.1)	4.7 (0.0)
183	2,2′,3,4′,5,5′,6-	7.2	0.9	0.1	0.7 (0.1)	6.2 (3.5)	0.4 (0.1)	3.7 (0.1)
187	2,2′,3,4,4′,5′,6-	7.17	2.0	0.2	0.8 (0.1)	7.1 (1.3)	0.5 (0.1)	4.1 (0.0)
194	2,2′,3,3′,4,4′,5,5′-	7.8	0.6	0.02	0.3 (0.1)	9.7 (3.1)	0.2 (0.0)	5.3 (0.2)

TABLE 1 (Continued)

IUPAC no.	structure	log K_{OW}	water concn whole (ng/L)	water concn dissolved (ng/L)[b]	SPMD $k_{1(S)}$ uncorrected for TOC (L/g·d)[c]	SPMD $k_{1(S)}$ corrected for TOC (L/g·d)[b,c]	trout $k_{1(F)}$ uncorrected for TOC (L/g·d)[b]	trout $k_{1(F)}$ corrected for TOC (L/g·d)[b,c]
199	2,2′,3,3′,4,5,5′,6′-	7.62	0.6	0.03	0.4 (0.1)	9.0 (3.2)	0.3 (0.1)	7.2 (0.3)
201	2,2′,3,3′,4,5′,6,6′-	7.27	0.2	0.02	0.4 (0.1)	4.0 (6.3)	na	na
207	2,2′,3,3′,4,4′,5,6′6′-	7.74	0.2	0.01	0.06 (0.0)	1.7 (0.8)	na	na
tPCBs		6.38[e]	4933[f]	3682[f]	1.1[e]	3.1[e]	0.5[e]	1.6[e]

[a] Duration of exposure, 28 days; av water temp, 11.8 °C; TOC estimate, 0.5 mg/L; $n = 12$ for water concentration values. [b] Corrected for 0.5 mg/L TOC adsorption. Assumption: $K_{OC} = K_{OW}$. K_{OW} values estimated by Hawker and Connell (*20*). [c] Calculations of $k_{1(S)}$ and $k_{1(F)}$ are based on averages of 7, 14, and 28 day values; $n = 3$ for each time period. [d] Not applicable, unresolvable peak. [e] Values for total PCBs (tPCBs) are averages of individual congener values. [f] Values are sums of individual congener values.

comparisons (*3*, *32*). However, this is not surprising because, unlike the surface water exposures, no food or visible particulate matter was available for fish ingestion.

An apparent reduction in the SPMD and fish uptake rates at log $K_{OW} \geq 6$ has been noted in a number of studies (*10*, *33*). We also observed an overall decline in k_1 values as K_{OW} values became very large, but this phenomenon was not observed when TOC partitioning was taken into account. The apparently lower uptake rates of the more lipophilic compounds (based on log K_{OW}) by fish and SPMDs may be due to extremely limited water solubility coupled with increased binding to the TOC in the water, both of which limit the amount of chemical contacting the membrane surface. When present at trace levels in an environment with competing organic carbon phases, the amount of truly dissolved residues is vanishingly small. In many cases, the volume of water exchanged at the SPMD membrane surface and at the gill integument appears to be mediated by system flow/turbulence (aqueous boundary layer control) and ventilation volume, respectively. On the basis of the boundary layer theory, the first-order uptake rate constant (i.e., the volume of water cleared of chemical per unit time by 1 g of SPMD or fish) would decline only slightly as PCB K_{OW} increases because of the small decrease in diffusivity of highly chlorinated congeners. Growth dilution by fish can also play a role in the observed reduction in uptake rates of high K_{OW} PCBs, but fish in this study were not fed. Concentrations of PCBs were present in the spring water that were much higher than all but the most heavily PCB-contaminated surface waters while TOC levels were very low. Thus, detection of high K_{OW} congeners in water was feasible, and the results, based on TOC corrections, indicated a general rise in $k_{1(F)}$ and $k_{1(S)}$ with degree chlorination (and the attendant rise in K_{OW}) without the previously observed discontinuity at $K_{OW} \geq 6$.

Another factor that may contribute to a discontinuity at $K_{OW} \geq 6$ is membrane (SPMDs and fish gills) permeability limitations. However, membrane permeability limitations should not be a factor for PCBs. Examination of the molecular dimensions of PCB congeners, using the convention described by Sander and Wise (*34*) shows that the breadths of high K_{OW} PCB molecules are <9 Å, which is less than the proposed maximal (transcient) pore diameter in low-density polyethylene and gill integuments. Also, the biphenyl bond allows conformational and rotational freedom for most congeners, which may increase their polymer permeability. Earlier studies (*10*) observed a reduction in SPMD uptake rates correlated with high K_{OW} polycyclic aromatic hydrocarbons (PAHs). Unlike large molecular weight fused-ring (rigid) PAHs with breadths ≥9 Å, impedance to the mass transfer of high K_{OW} PCBs through the SPMD membrane and the lipoidal region of the gill integument of fish should be lower.

Since the uptake rates of the dissolved PCBs detected in this study are likely controlled by the aqueous boundary layer, extrapolation of our data to SPMD exposures under difficult

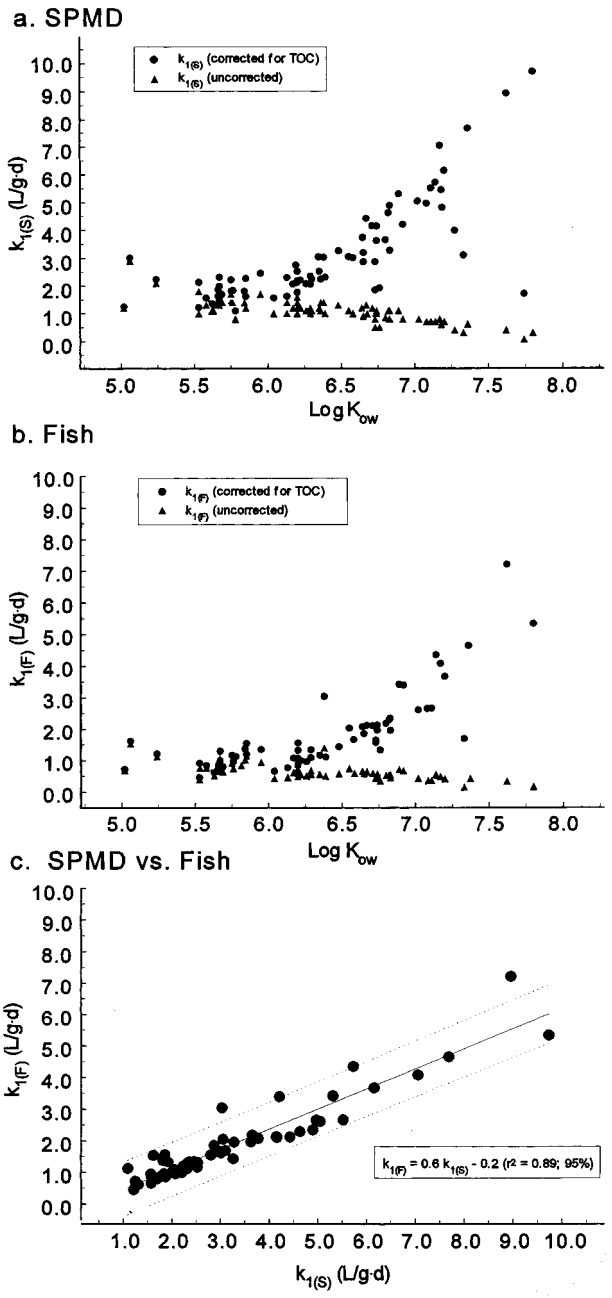

FIGURE 1. (a) Relationship of SPMD uptake rate constants ($k_{1(S)}$) to log K_{OW}. (b) Relationship of brown trout uptake rate constants ($k_{1(F)}$) to log K_{OW}. (c) Comparison of SPMD and brown trout uptake rate constants. Dotted lines indicate 95% confidence interval. Corrected values assume 0.5 mg/L total organic carbon and log $K_{OW} \cong K_{OC}$.

flow/turbulence regimes would be inappropriate without information on the magnitude of hydrodynamic effects. Booij et al. (*5*) has found as much as a 3−4-fold increase in SPMD PCB sampling rate when flow velocity was increased from 1 to 30 cm s. In our exposure, the linear flow velocity at the SPMD membrane was only ~0.01 cm s^{-1}, which is relatively quiescent when compared to many aquatic systems. Thus, the uptake rate data generated in this study can only be directly applicable to field exposures in quiescent environments. However, the use of a permeability reference compound (PRC) as described by Huckins et al. (*6*, *8*) should enable investigators to adjust k_1 values given in this report to values appropriate for a wide variety of study conditions. Based on the K_{OW} and k_1 of congener 006, a k_2 of 0.04 t^{-1} is estimated. The use of deuterated congener 006 in future studies as a PRC should permit correction of PCB k_2 for specific environments as described by Huckins et al. (*6*).

The results of this study indicate that, for unmetabolized compounds, uptake rates of PCBs by brown trout and SPMDs are similar to within a factor of 2 throughout a 500-fold range in K_{OW} values. These data strongly suggest that SPMDs closely mimic the uptake of PCBs across fish gills when fish are deprived of food. The initially uncontaminated brown trout had accumulated body burdens of 118 μg/g of total PCBs by the end of the exposure, as compared to 203 μg/g of total PCBs by the SPMDs. If uptake rate information (R_S or k_1) is available for a compound, its dissolved water concentration may be estimated from its measured concentration in an SPMD using eqs 5 and 6. The total water concentration ($C_{W(tot)}$)of the compound can be estimated from its measured SPMD concentration and the measured TOC concentration of the water by combining eqs 4 and 5:

$$C_{W(tot)} = \left(1 + \frac{m_{OC}K_{OC}}{m_W}\right)\frac{C_S m_S}{R_S t} \quad (7)$$

or by combining eqs 4−6:

$$C_{W(tot)} = \left(1 + \frac{m_{OC}K_{OC}}{m_W}\right)\frac{C_S}{k_{1(S)}t} \quad (8)$$

Likewise, total water concentrations of unmetabolized compounds may be estimated from concentrations in fish, if the compound's $k_{1(F)}$ is known and is substituted for $k_{1(S)}$ and if tissue concentration (C_F) is substituted for C_S in eq 8. However, unlike SPMDs, tissue concentrations of some chemicals in different species, sexes, and ages of fish are known to vary considerably, limiting the accuracy of the extrapolation of water concentrations from fish tissues.

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