Use of Equilibrium Partitioning Theory to Determine Route(s) of Chlorinated Hydrocarbon Uptake in Hornyhead Turbot

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ABSTRACT

Fish at various locations in southern California coastal waters are known to be contaminated with persistent chlorinated hydrocarbons. The possible route(s) of uptake of these contaminants, however, are not well understood. In this article, we use the equilibrium partitioning theory (EPT) to determine the possible accumulation pathways of dichloro-diphenyl-trichloroethane (DDT), its metabolites (p,p'- and o,p'-DDT, DDD, and DDE; designated as DDTs hererinafter), and polychlorinated biphenyls (PCBs) in hornyhead turbot, a demersal fish. Water, surface sediments, polychaetes, and hornyhead turbot were collected in October/November 1995 and April/May 1996 from four near-shore locations. The distribution of DDTs and PCBs in surface sediments, polychaetes, and muscle tissues of hornyhead turbot was generally in compliance with the EPT, but large variations were noted for individual partitioning coefficients. Partitioning between water and other compartments (surface sediment, hornyhead muscle tissue, and hornyhead liver tissue), characterized by $\log K_{sw}$, $\log K_{mw}$, and $\log K_{lw}$, respectively, generally covaried with $\log K_{ow}$ (octanol-water partitioning coefficient). Despite a wide range of fluctuations, measured values of $\log K_{sw}$, $\log K_{mw}$, and $\log K_{lw}$ were consistently lower than those of $\log K_{ow}$. Discrepancies between the field data and the EPT, where noted, were likely attributable to the overestimation of the dissolved organics concentrations, nonequivalence of organic carbon (OC) in sediment and lipids in biota, and steric effects. Although a stepwise increment in concentrations of DDEs and DDDs was observed in the food chain of hornyhead turbot, the differences were not significant. Taken together, the results suggest that accumulation of chlorinated hydrocarbons in hornyhead turbot occurs primarily via direct uptake of contaminants from water by the equilibrium partitioning process. Additional uptake of contaminants from food does not appear to amplify body burdens significantly.

INTRODUCTION

In southern California, a number of local and national environmental agencies have used hornyhead turbot as a prototype to monitor the temporal trend for bioaccumulation of trace metals and chlorinated hydrocarbons in coastal waters (Varanasi *et al.* 1989, Mearns *et al.* 1991, CLAEMD 1992, CSDOC 1992). Hornyhead turbot, *Pleuronichthys verticalis*, is a demersal flatfish that lies partially buried in the sediment and feeds primarily on bivalves and sedentary tube-dwelling polychaetes such as *Diopatra ornata*, *Pista alata*, and *Paraprionospio pinnata*. The hornyhead turbot population is widespread in areas surrounding the 60-m depth contour in the Southern California Bight (SCB) (CLAEMD 1995). In addition, lipid content in hornyhead turbot fluctuates less than that in other species due to the active productivity of hornyhead turbot throughout the year (Goldberg 1982).

Recent studies indicated that chlorinated hydrocarbons remain abundant in hornyhead turbot collected

from near-shore areas of the SCB, despite the reduction in mass emissions of chlorinated hydrocarbons to the coastal environment from historical discharges (Raco-Rands 1997). For example, the mean wet weight concentration of total DDTs (sum of o,p'- and p,p'-DDT, DDD, and DDE) was 2.5μg/g in muscle tissues and 28 μg/g in liver tissues of hornyhead turbot collected in Spring 1995 near the outfall of the Joint Water Pollution Control Plant (JWPCP), operated by the County Sanitation Districts of Los Angeles County (CSDLAC) (Gluckman-Peskind *et al.* 1995).

Demersal fish such as hornyhead turbot have two principal routes for uptake of toxic chemicals from contaminated areas. The first route involves the uptake of contaminants from water directly through passive diffusion of the freely dissolved phase present in the water column (Oliver and Niimi 1983, Connolly and Pedersen 1988). The second route is through consumption of contaminated food (Thomann and Connolly 1984).

One approach to differentiating between these two pathways is the use of the EPT. The EPT is based upon the assumption that the distribution of contaminants in various interacting phases is dictated primarily by rapid and continuous chemical exchange processes (Shea 1988). At equilibrium, the fugacity of a chemical, as defined below, in all of the phases must be equal (Bierman 1990). If the accumulation of contaminants in hornyhead turbot is in equilibrium with those in other media, the EPT predicts that the first route of uptake is likely. On the other hand, if additional uptake via food chain transfer takes place, higher chemical fugacity in hornyhead turbot than in other compartments may be observed. In this study, we applied the EPT to determine the principal route(s) for uptake of PCBs and DDTs in hornyhead turbot.

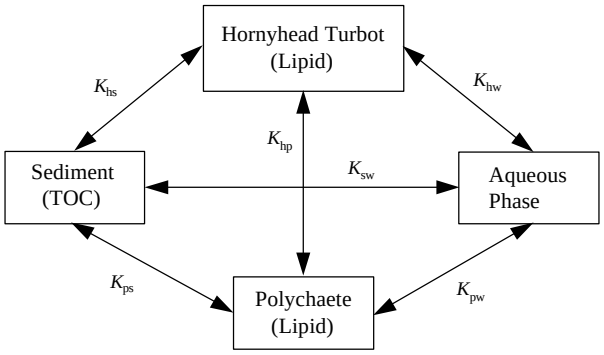
Equilibrium Partitioning Theory

Partitioning of hydrophobic organics within the food chain of hornyhead turbot is conceptually demonstrated in Figure 1. Under equilibrium conditions, the fugacity, *F*, of a hydrophobic chemical is identical in all of the phases (Bierman 1990), i.e.,

$$F_s = F_p = F_l = F_m = F_w \qquad (1)$$

where the subscripts s, p, l, m, and w refer to sediment, polychaete, hornyhead turbot liver, hornyhead turbot muscle, and water (truly dissolved phase), respectively. The fugacity in each phase can be related to chemical concentration, *C*, and fugacity capacity, *Z* (Connolly and Pedersen 1988), by $F = C/Z$. Furthermore, *Z* in water is an inverse of the Henry's law constant, *H* (Campfens and Mackay 1997), i.e.,

FIGURE 1. A conceptual model of phase partitioning of hydrophobic organic chemicals in various environmental compartments.



$$Z_w = 1/H \qquad (2)$$

In sediment and biota, it is widely assumed that the partitioning media for hydrophobic organics is OC and lipid, respectively. In laboratory experiments, octanol is normally used as a convenient matrix considered equivalent to OC and lipid. Hence, the octanol-water partitioning coefficient, K_{ow}, equals the ratio of the fugacity capacities in the organic and water phases reaching equilibrium:

$$K_{ow} = C_o/C_w = Z_o/Z_w \qquad (3)$$

By combining Equations (2) and (3), the fugacity capacities in sediment and tissues of polychaete and hornyhead turbot can be written as:

$$Z_s = f_s K_{ow}/H \qquad (4)$$
$$Z_p = f_p K_{ow}/H \qquad (5)$$
$$Z_l = f_l K_{ow}/H \qquad (6)$$
$$Z_m = f_m K_{ow}/H \qquad (7)$$

where *f* indicates the fraction of either OC in sediment (f_s) or lipid in tissues of polychaete (f_p) and hornyhead turbot liver or muscle tissues (f_l or f_m, respectively). Finally, the partitioning between hornyhead turbot (both liver and muscle tissues) and sediment, polychaete, and water can be described using Equations (1) - (7):

$$K_{ls} = (C_l/f_l)/(C_s/f_s) = 1 \qquad (8)$$
$$K_{ms} = (C_m/f_m)/(C_s/f_s) = 1 \qquad (9)$$

$$K_{lp} = (C_l/f_l)/(C_p/f_p) = 1 \quad (10)$$
$$K_{mp} = (C_m/f_m)/(C_p/f_p) = 1 \quad (11)$$
$$K_{ps} = (C_p/f_p)/(C_s/f_s) = 1 \quad (12)$$
$$K_{sw} = (C_s/f_s)/C_w = K_{ow} \quad (13)$$
$$K_{lw} = (C_l/f_l)/C_w = K_{ow} \quad (14)$$
$$K_{mw} = (C_m/f_m)/C_w = K_{ow} \quad (15)$$

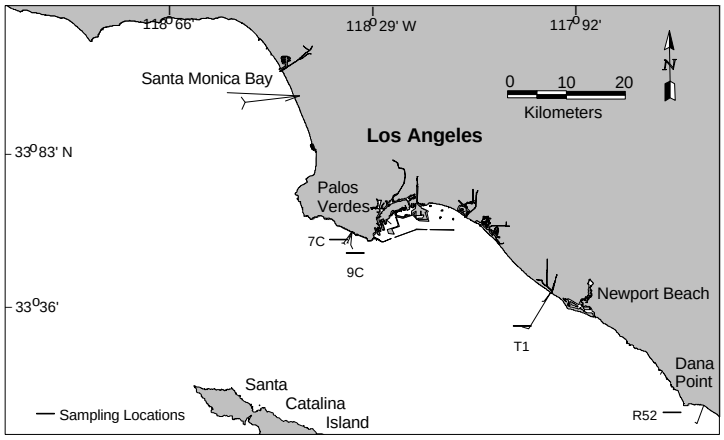
Equations (8) - (15) will be used to analyze field data. If the EPT is followed strictly, Equations (8) - (12) suggest that K_{ls}, K_{ms}, K_{lp}, K_{mp}, and K_{ps} are unity and independent of K_{ow}, an indicator of hydrophobicity for a chemical compound. In addition, a direct correlation between K_{sw} or K_{lw} or K_{mw}, and K_{ow} is expected if the EPT is followed, as shown in Equations (13) - (15).

METHODS

Sample Collection

Samples from four different media (surface sediment, water column, polychaete, and hornyhead turbot) were collected in October/November 1995 (henceforth the October 1995 sampling period) and April/May 1996 (henceforth the April 1996 sampling period). These samples were collected at Stations 7C and 9C near the JWPCP outfall; Station T1 near the outfall of Orange County Sanitation District (OCSD), formerly known as County Sanitation Districts of Orange County; and a reference station, R52, off Dana Point (Figure 2). Samples of the different media specifically collected at each station during each sampling period are listed in Table 1.

FIGURE 2. Sampling stations off Palos Verdes Shelf, Huntington Beach, and Dana Point, California.



Water column samples were collected approximately 1 m from the sea floor using an Infiltrex 100 water sampler (Axys Environmental Systems Ltd., Sidney, British Columbia, Canada). Suspended particles were filtered with glass fiber filters (142 mm GF/F filters with 0.7 µm pore size), while dissolved organics were retained on XAD-II resins packed inside a Teflon column. Detailed operational procedures were described previously (Tran and Zeng 1997). The Teflon columns were wrapped in aluminum foil, and then cooled with ice during transport to the laboratory.

Sediments were collected using a modified 0.1 m^2 chain-rigged Van Veen grab (Stubbs *et al.* 1987). Sediments from the top 2-cm layer were collected and transferred into precleaned glass jars.

Polychaetes including *Diopatra ornata*, *Pista alata*, and *Paraprionospio pinnata* were obtained by passing sediments through a 1.0-mm screen. The polychaetes were washed thoroughly with seawater to remove attached sediment. They were then stored in precleaned glass jars and chilled in an ice chest during transport to the laboratory, where they were kept frozen at -20° C.

Fish were collected opportunistically by trawling at 60-m depth using 7.6-m headrope semi-balloon otter trawls with 1.25-cm cod end mesh. Trawls were towed for 10 min (bottom time) at 0.8-1.2 m/sec (1.5-2.4 knots). Once on board, the fish were wrapped in aluminum foil and placed in plastic bags. All samples were chilled in an ice chest and transported to the laboratory. Fish were dissected immediately or on the following morning. Six hornyhead turbot from each station were dissected and analyzed individually. Whenever possible, sexually mature fish were selected with an equal number of males and females. Muscle and liver tissues from individual fish were stored separately in glass vials and kept frozen at -20° C until analysis.

TABLE 1. List of locations and sample media collected. S = surface sediment, W =water column, P = polychaete, and H = hornyhead turbot.

	Oct. '95	Apr. '96
7C	S,W,P,H	S,W,P,H
9C	S,P,H	S,P,H
T1	S,W,P,H	S,W,P,H
R52	S,H	S,W,P,H

Sample Processing and Extraction

All of the samples were spiked with appropriate surrogate standards prior to extraction. Teflon columns retaining dissolved organics were eluted consecutively with 200 mL of methylene chloride and methanol at a flow rate of 5 mL/min. The methanol fraction was back-

extracted three times with methylene chloride (50 mL each extraction). Sediment samples of approximately 10-40 g were extracted three times (16, 6, and 16 h, respectively) with methylene chloride (100 mL each extraction) using a roller table. Each tissue sample (ungutted polychaetes, hornyhead muscles, and hornyhead livers) was homogenized thoroughly with a glass rod and weighed in a glass beaker. Approximately 20 mL of acetonitrile was added to the beaker. The mixture was extracted three times with 10 mL of hexane each extraction using a Polytron high-speed homogenizer (Zeng *et al.* 1997).

Extracts from the same sample were combined and concentrated using a rotary evaporator at 30° C and 650 mm Hg vacuum pressure. Activated copper granules were added to the extract to remove sulfur (in the dark, overnight). The extract was further concentrated to 1 mL under gentle nitrogen flow. Approximately 3 to 5 µL of the hexane extract was transferred to an aluminum boat that had been preweighed on a microbalance. The solvent was allowed to evaporate until a constant weight was obtained. The weight difference was used to determine the extractable hydrocarbon content (also defined as lipid content for biological samples). Measurements were performed in triplicate to obtain an average value for each sample.

Based upon the extractable hydrocarbon content, an appropriate portion of each extract was loaded onto a 1:2 alumina:silica gel glass column for clean-up/fractionation. The column was first eluted with 15 mL of dry hexane and the eluate was discarded. The PCBs and DDTs were then eluted with 5 mL of dry hexane and 30 mL of a 30/70 mixture of methylene chloride/hexane. The combined extract was concentrated to 1 mL using a Zymark TurboVap 500 (Zymark Corporation, Hopkinton, MA). An appropriate amount of internal standards were added to the extract prior to instrumental analysis.

Instrumental Analysis

Measurements of Total Organic Carbon

Total organic carbon (TOC) in sediments was measured using the method described previously (SCCWRP 1994a). Dry sediment (~30 mg) was weighed in a silver capsule and exposed to concentrated HCl vapor for at least 18 h to remove inorganic carbon. The acidified sample was subsequently dried at 60° C overnight and crimped in a tin capsule. The measurement was conducted using a Carlo Erba 1108 CHN elemental analyzer.

Measurements of Chlorinated Hydrocarbons

Quantitation of PCBs and DDTs was performed using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC) equipped with a ^{63}Ni electron capture detector and a 60 m × 0.25 mm i.d. (0.25 mm film thickness) DB-5 column (J&W Scientific, Folsom, CA). One µL of each sample was injected by an HP 7673 autosampler in split/splitless mode with a 1-min solvent split time. The column temperature was programmed from 90° C to 180° C at 6° C/min, followed by an increase to 290° C at 1° C/min. High-purity helium was used as carrier gas at a flow rate of 2 mL/min (90° C) and ultra-high-purity nitrogen was the makeup gas at 30 mL/min. Both injector and detector were maintained at 280° C. Data were acquired and processed using a Perkin Elmer Nelson Turbochrom 3.3 data system running on an IBM compatible PC and Perkin Elmer Nelson 900 Series interface unit. A total of 15 organochlorine pesticides and 122 PCB congeners were included in the analyses. Individual congeners were detected and quantified using the congener-specific method. Additional details of the experimental conditions including gas chromatography/mass spectrometry (GC/MS) confirmation of peak identification were described elsewhere (SCCWRP 1994b, Zeng *et al.* 1997).

Data Analysis

To apply the EPT based upon Equations (8) - (13), partitioning coefficients for individual chlorinated hydrocarbons were calculated from measured concentrations in different compartments. Although our list of analytes included 15 chlorinated pesticides and 122 PCB congeners, a smaller number of target analytes were detected in the samples. Therefore, partitioning coefficients will be reported only for target analytes detected. For aqueous (overlying water) samples, C_w (ng/L) of each individual chlorinated hydrocarbon was obtained as the average of two replicate measurements. A similar method was also used to obtain C_p (ng/g wet weight) for polychaete. For sediment, the concentration of each analyte, C_s (ng/g dry weight) was an average of three measurements. For hornyhead turbot, since the number of detectable PCB congeners varied significantly among hornyhead turbot individuals, only the muscle and liver tissue concentrations (ng/g wet weight) in a specific individual with the largest number of detectable PCB congeners were used. The TOC- and lipid-based concentrations were used to obtain various partitioning coefficients as shown in Equations (8) - (13). The K_{ow} values were taken from the literature (DDTs: Gossett *et al.* 1983; PCB congeners: Hawker and Connell 1988).

RESULTS

Distribution of Contaminants

The TOC in surface sediments (0-2 cm) and lipid content in polychaetes and hornyhead turbot tissues are presented in Table 2. In general, no seasonal variation in TOC and lipid content was evident at a specific location. Conversely, TOC and lipid contents varied significantly among different locations or compartments. The TOC content was highest in the Station 7C sediments (3.16±0.02%) and lowest in the Station T1 sediments (0.35±0.07%). The TOC contents were consistently higher in Station R52 sediments than in Station T1 sediments, although Station T1 is near the OCSD outfall. At a specific location, hornyhead turbot liver tissues contained the highest lipid content, while hornyhead turbot muscle tissues contained the lowest lipid content. For hornyhead turbot liver tissues and polychaetes, the lipid content by station was in the order of 7C>9C>T1>R52. Lipid content was surprisingly similar in muscle tissue samples, with essentially no statistical difference among the four groups of samples.

For chlorinated pesticides, only the main DDT metabolites (p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD) were detected. Concentrations of DDEs+DDDs (lipid or TOC normalized) were highest in the liver tissues of hornyhead turbot compared to other compartments and lowest in surface sediments, while hornyhead turbot muscle tissues and polychaetes contained similar amounts of DDEs+DDDs (Figure 3). For a given compartment, concentrations of DDEs+DDDs were higher at Stations 7C and 9C than at Stations T1 and R52. For PCBs, Stations 7C and R52 had the highest and lowest number of detectable PCB congeners, respectively.

Partitioning of Chlorinated Hydrocarbons in the Food Chain of Hornyhead Turbot

The correlation between K_{ow} and each of K_{sw}, K_{mw}, and K_{lw} for the 7C sediments and hornyhead turbot (both liver and muscle tissues) collected in the April 1996 sampling period was obtained for all detectable DDT components and PCB congeners (Figure 4). Linear regression analyses on these data yielded the following relationships:

$$\log K_{sw} = 0.78 \log K_{ow} - 0.31 \quad (r^2=0.34) \quad (16)$$

$$\log K_{mw} = 0.46 \log K_{ow} + 2.01 \quad (r^2=0.41) \quad (17)$$

$$\log K_{lw} = 0.70 \log K_{ow} + 0.59 \quad (r^2=0.39) \quad (18)$$

TABLE 2. Total organic carbon (percent dry weight) in sediments and lipid content (percent wet weight) of tissues of polychaetes and hornyhead turbot.

	Sediments		Polychaetes		Hornyhead Turbot			
					Muscles		*Livers*	
	Oct. '95	Apr. '96	Oct. '95	Apr. '96	Oct. '95	Apr. '96	Oct. '95	Apr. '96
7C	3.16 ± 0.02	3.23 ± 0.01	1.71 ± 0.06	1.78 ± 0.09	0.42 ± 0.17	0.25 ± 0.02	11.05 ± 4.48	11.43 ± 6.56
9C	1.46 ± 0.01	1.44 ± 0.04	1.34 ± 0.01	1.78 ± 0.04	0.33 ± 0.15	0.44 ± 0.33	10.18 ± 4.73	11.92 ± 3.02
T1	0.35 ± 0.07	0.32 ± 0.01	0.99 ± 0.14	1.12 ± 0.13	0.27 ± 0.09	0.32 ± 0.06	8.13 ± 3.92	6.10 ± 3.07
R52	0.69 ± 0.06	0.66 ± 0.01	NA[a]	0.3[b]	0.28 ± 0.06	0.28 ± 0.04	6.69 ± 3.55	5.56 ± 4.08

[a] Not available due to no sample was collected.
[b] Only one replicate was analyzed.

Other partition coefficients, including K_{ms}, K_{ls}, K_{ps}, K_{mp}, and K_{lp}, were also calculated for samples collected from Stations 7C, 9C, T1, and R52 (Table 3).

At Station 7C, the average log values for all partition coefficients were close to zero (Table 3), in reasonable agreement with the EPT. However, individual partitioning coefficients varied by a wide range, as indicated by large standard deviations associated with all the average values.

The numbers of detected PCB congeners in the Station 9C samples were generally smaller than those in the Station 7C samples. The average values of $\log K_{ms}$, $\log K_{ps}$, and $\log K_{mp}$ were very close to zero (Table 3). However, the average $\log K_{ls}$ and $\log K_{lp}$ values were slightly higher than zero.

No PCB congeners were detectable in the water samples collected from Stations T1 and R52. Only DDT metabolites were detected in the water samples from these stations. The total numbers of PCBs and DDTs detected in other compartments from Stations T1 and R52 were much smaller than those from Stations 7C and 9C (Table 3). Interestingly, individual values of $\log K_{ms}$,

FIGURE 3. Distribution of total DDEs and DDDs (ng/g TOC for sediment samples and ng/g lipid for biota samples) in the food chain of hornyhead turbot. L = hornyhead turbot livers, M = hornyhead turbot muscles, P = polychaetes, S = sediments.

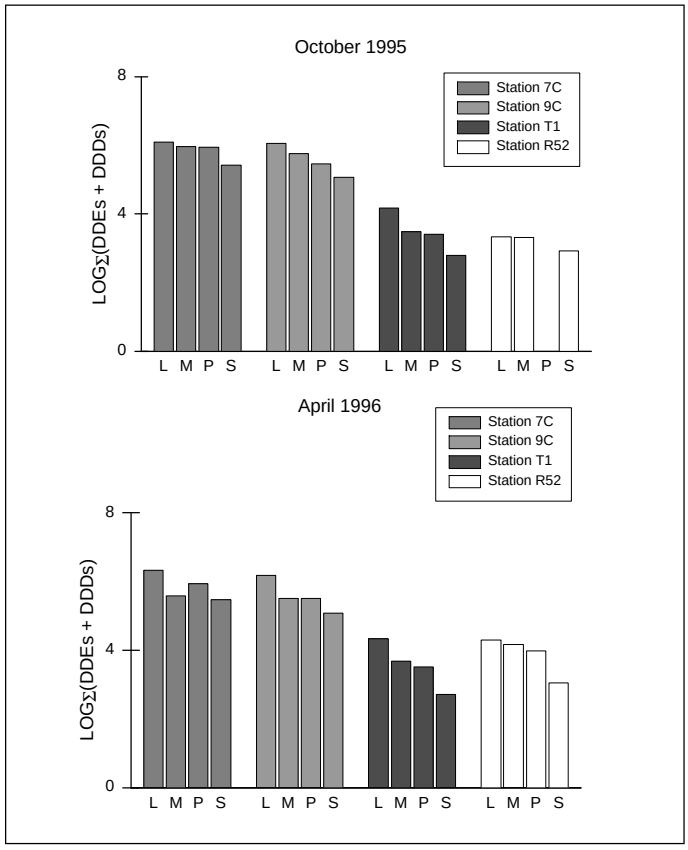
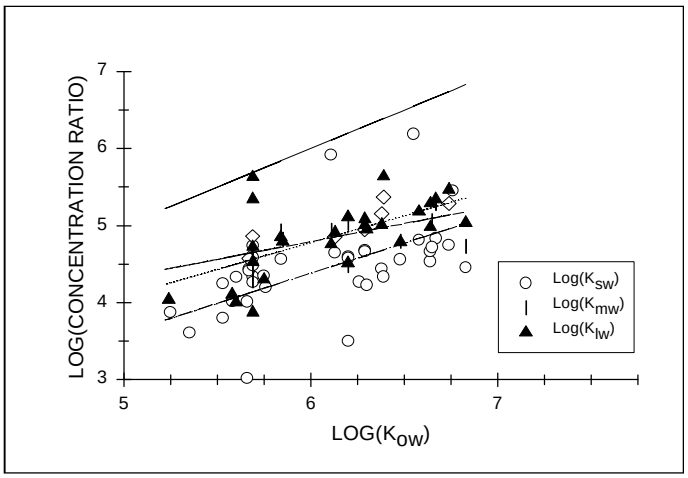


FIGURE 4. LogK_{ow} dependence of logK_{sw}, logK_{mw} and logK_{lw} measured for different organochlorines at Station 7C in the April 1996 sampling period.



logK_{ls}, logK_{ps}, and logK_{lp} for p,p'-DDE were all higher than zero (Table 3).

DISCUSSION

Evaluation of Field Data Using Equilibrium Partitioning Theory

Two sets of data can be evaluated using the EPT under field conditions. The first set of data comprises partitioning coefficients associated with sediments, polychaetes, and hornyhead tissues; these data can be examined using Equations (8) - (12). The second set of data contains coefficients for partitioning between water and sediment or hornyhead tissues and can be examined using Equations (13) - (15).

The near-zero values of the five partitioning coefficients (K_{ms}, K_{ls}, K_{ps}, K_{mp}, and K_{lp}) for a number of chlorinated hydrocarbon compounds, at four near-shore locations and in two sampling seasons (Table 3), strongly suggest that partitioning of DDT and PCB congeners in the system of sediments-polychaetes-hornyhead tissues generally conforms with the EPT. In addition, virtually no difference was observed between the average log ratios for chlorinated hydrocarbons with logK_{ow} values of 5.22-6.00 and those with higher logK_{ow} values (6.00-7.36). This finding indicates no apparent dependence of uptake of organic contaminants on their hydrophobicities. Similar results were reported for benthic organisms (Bierman 1990). The direct correlation between concentrations in sediments and in polychaetes or hornyhead turbot tissues can be beneficial for sampling and analytical designs in general; chemical concentrations in biota can be inferred from those in sediments, which are relatively easier than biota to collect and analyze.

The correlation between logK_{ow} and each of logK_{sw}, logK_{lw}, and logK_{mw} (Equations (13)-(15)) determines whether the field data can be described by the EPT. Linear regression analyses on one set of samples (Station 7C samples collected in the April 1996 sampling period) all yielded slopes less than unity (Equations (16)-(18)) with an extremely wide range of variation (Figure 4). However, the range of variation observed in these samples is similar to or more variable than results obtained from other field data (Bierman 1990, Connor 1984). Although no similar analyses were performed on data obtained for other stations due to the lack of sufficient numbers of detectable organochlorines, the field data regarding the partitioning between water and sediment or hornyhead tissues at Station 7C was in qualitative agreement with predictions by the EPT.

The relationships shown in Figure 4 indicate that all the concentration ratios from the Station 7C samples were smaller than the corresponding logK_{ow} values. This

TABLE 3. Average values of partition coefficients for detected chlorinated hydrocarbons at Stations 7C, 9C, T1, and R52.

		7C		9C	
	$\log K_{ow}$	Oct. '95	Apr. '96	Oct. '95	Apr. '96
$\log K_{ms}$	5.22 - 7.36	0.23[a] ± 0.43[b] (9)[c]	0.23 ± 0.39 (19)	0.15 ± 0.45 (4)	0.14 ± 0.41 (4)
	5.22 - 6.00	0.24 ± 0.34 (4)	0.15 ± 0.11 (7)	0.15 ± 0.44 (4)	0.14 ± 0.41 (4)
	6.00 - 7.36	0.22 ± 0.53 (5)	0.29 ± 0.49 (12)	NA[d]	NA
$\log K_{ls}$	5.22 - 7.36	0.46 ± 0.53 (10)	0.34 ± 0.47 (28)	0.84 ± 0.16 (4)	0.71 ± 0.38 (5)
	5.22 - 6.00	0.63 ± 0.20 (4)	0.19 ± 0.48 (9)	0.84 ± 0.16 (4)	0.71 ± 0.44 (4)
	6.00 - 7.36	0.35 ± 0.67 (6)	0.41 ± 0.47 (19)	NA	0.67 (1)
$\log K_{ps}$	5.22 - 7.36	0.17 ± 0.28 (10)	0.14 ± 0.20 (30)	0.24 ± 0.13 (4)	0.10 ± 0.31 (5)
	5.22 - 6.00	0.19 ± 0.28 (4)	0.17 ± 0.15 (12)	0.24 ± 0.13 (4)	0.11 ± 0.36 (4)
	6.00 - 7.36	0.15 ± 0.30 (6)	0.11 ± 0.22 (18)	NA	0.05 (1)
$\log K_{mp}$	5.22 - 7.36	0.09 ± 0.27 (17)	0.17 ± 0.43 (23)	0.26 ± 0.72 (15)	0.08 ± 0.22 (18)
	5.22 - 6.00	0.09 ± 0.11 (7)	0.10 ± 0.36 (10)	-0.02 ± 0.26 (6)	0.15 ± 0.17 (8)
	6.00 - 7.36	0.09 ± 0.35 (10)	0.23 ± 0.48 (13)	0.45 ± 0.88 (9)	0.03 ± 0.24 (10)
$\log K_{lp}$	5.22 - 7.36	0.29 ± 0.49 (34)	0.18 ± 0.39 (30)	0.56 ± 0.41 (27)	0.42 ± 0.23 (35)
	5.22 - 6.00	0.06 ± 0.44 (16)	-0.02 ± 0.37 (11)	0.42 ± 0.38 (8)	0.45 ± 0.26 (10)
	6.00 - 7.36	0.49 ± 0.45 (18)	0.29 ± 0.37 (19)	0.61 ± 0.42 (19)	0.41 ± 0.22 (25)

[a]Average value of partition coefficients obtained for organochlorines with $\log K_{ow}$ in the specified range.
[b]Standard deviation of partition coefficients obtained for organochlorines with $\log K_{ow}$ in the specified range.
[c]Number of individual partition coefficents included in the statistical analysis = Number of detectable DDTs and PCBs in the relevant compartments.
[d]Not available due to the nondetectability of organochlorines with $\log K_{ow}$ in the specified range in the relevant compartments.

correlation suggests that concentrations of chlorinated hydrocarbons in the overlying water exceeded the equilibrium concentrations expected from the EPT. In addition, the magnitude of deviation from equilibrium was not uniform for all detectable compounds (Figure 4). Slightly larger deviations were observed for compounds with high $\log K_{ow}$, suggesting they were more "soluble." This trend appears to contradict the expectation based upon hydrophobicity (i.e., substances with higher K_{ow} are generally more difficult to dissolve in water than those with lower K_{ow}). An explanation is given below.

In the aqueous phase, only truly "dissolved" chemicals are bioavailable. Any fraction associated with dissolved organic matter (DOM) or colloidal material is generally considered unavailable for uptake by organisms via diffusion. Black and McCarthy (1988) investigated the effects of DOM on the uptake of hydrophobic organics by fish and concluded that organics bound to DOM did not diffuse across the gill membrane of rainbow trout. In our studies, the sampled sea- water, after passing through the filters with a 0.7-µm pore size, may still contain a large amount of organics bound to DOM or colloidal material. This fraction of organics may be retained on the XAD-II resin and subsequently extracted. Hence, concentrations of truly dissolved organics may have been overestimated, resulting in lower-than-expected values for the partitioning coefficients (Figure 4). In open waters, a large fraction (50-80%) of dissolved hydrophobic organics could be bound to DOM (Yin and Hassett 1986, Oliver and Niimi 1988). In the presence of DOM, the solubility of organics increases with K_{ow} (Chiou *et al.* 1986). Also, the actual concentration, which is available for uptake, of a chemical with $\log K_{ow}$ greater than 6.5 was lower than its total concentration in water (Gobas *et al.* 1989). These factors, combined, may have resulted in an increased difference between $\log K_{ow}$ and log-based partitioning coefficients for PCB congeners with increasing K_{ow}.

Factors Influencing the Consistency Between Field Data and the EPT

One inherent factor that influences the consistency between field data and the EPT is the equivalency assumption for OC in sediment, lipid in biota, and octanol. The equivalency assumption states that partitioning of hydrophobic compounds between sediment

T1		R52	
Oct. '95	Apr. '96	Oct. '95	Apr. '96
0.69 (1)	1.01 (1)	0.4 (1)	1.24 (1)
0.69 (1)	1.01 (1)	0.4 (1)	1.24 (1)
NA	NA	NA	NA
1.33 (1)	1.40 ± 0.32 (2)	0.41 (1)	0.69 ± 0.95 (2)
1.33 (1)	1.40 ± 0.32 (2)	0.41 (1)	0.69 ± 0.95 (2)
NA	NA	NA	NA
0.56 (1)	0.77 (1)	NA	1.28 ± 0.72 (2)
0.56 (1)	0.77 (1)	NA	1.28 ± 0.72 (2)
NA	NA	NA	NA
-0.09 ± 0.31(2)	0.05 ± 0.27 (2)	NA	0.48 (1)
0.12 (1)	0.25 (1)	NA	0.48 (1)
-0.31(1)	-0.14 (1)	NA	NA
0.17 ± 0.33 (7)	0.54 ± 0.46 (2)	NA	0.6 (1)
0.50 ± 0.38 (2)	0.54 ± 0.46 (2)	NA	0.6 (1)
0.03 ± 0.23 (5)	NA	NA	NA

and water or between biota and water can be regarded as equivalent to partitioning between octanol and water. However, the validity of this equivalency remains questionable. Opperhuizen *et al.* (1988) demonstrated that the rate of uptake via lipid membranes of biota was significantly different from that occurring via the octanol/water interface. In addition, Chiou (1985) showed that triolein-water partitioning coefficients correlated better with field data compared to octanol-water partitioning coefficients.

Another factor is stereochemistry. According to the EPT, concentration gradient is the driving force for diffusion of chemicals among phases, and no steric restriction is assumed (Bierman 1990). In reality, however, chemicals have to cross an external membrane to reach the interior of an organism. Stereochemistry is known to influence the uptake and bioaccumulation of PCBs in aquatic organisms (Shaw and Connell 1984). In general, planar PCB congeners were more efficiently adsorbed than those with more complex structures (Shaw and Connell 1984). Chemicals with relatively high K_{ow} often have unexpectedly low lipid solubility (Chessels *et al.* 1992), probably due to the same steric effects. Since our data set involves chlorinated hydrocarbon compounds that vary in molecular structure and size, it is not unexpected to have a wide range of differentiation between the field data and predictions from the EPT (Table 3 and Figure 4).

Possible Uptake Routes of Chlorinated Hydrocarbons by Hornyhead Turbot

Bioconcentration is a process by which chemicals are accumulated directly from water to aquatic organisms (Thomann 1989). Bioaccumulation, on the other hand, is defined as a process for accumulation of chemicals in aquatic organisms from all possible routes of uptake (Jager 1998). Under strictly equilibrium conditions, the EPT predicts that the fugacities in all interacting phases should be identical. Chemical concentrations are the same for individual tissues within an organism, as well as for different organisms regardless of their trophic levels (Connolly and Pedersen 1988).

For demersal fish such as hornyhead turbot that occupy a higher trophic level than benthic animals, food chain accumulation may result in biomagnification. Highly hydrophobic compounds are less likely to be found in the water phase in appreciable amounts (Mackay 1982); they are more likely associated with

particulate matter. The contaminant-bound particles may be a food source for filter-feeding or sediment-dwelling animals. When the contaminant-containing lipids of the prey (polychaetes) are digested in the gut of the predator (hornyhead turbot), higher chemical fugacity is established in the gut than in the rest of the predator's body. Since the lipid content is higher in the liver than in most of the other compartments of the fish (Table 2), a net flow of chemicals from the gut into the liver results. The final outcome is that concentrations in the predator are higher than those predicted by the EPT, based upon the assumption that uptake occurs primarily through the equipartitioning process. Higher bioaccumulation levels in the organisms occupying higher trophic positions as compared to those at the lower end of the same food chain were extensively investigated by other investigators (Connolly and Pedersen 1988, Oliver and Niimi 1988, Clark *et al.* 1990). Oliver and Niimi (1988) have also reported a stepwise increase in chemical concentrations of various PCB congeners in a benthic food chain consisting of phytoplankton, zooplankton, mysids, alewives, smelt, and salmonids in the Lake Ontario ecosystem. The total PCB concentrations in salmonids were nearly three orders of magnitude higher than those in their prey (alewives and smelt) (Oliver and Niimi 1988).

One possible transport route for contaminants is from the sediment up through the food chain to hornyhead turbot. Uptake through a food route often results in biomagnification (Thomann 1989). If biomagnification occurs, an increasing trend in the concentrations of contaminants from sediment to hornyhead turbot should be observed. This trend, however, was not apparent, as the values of log ratios were not significantly higher than zero (Table 3). In addition, if uptake through food is one of the major contributors to the contaminant burden in the biota, $\log K_{ms}$, $\log K_{ls}$, $\log K_{ps}$ should be higher for compounds with higher K_{ow} than those with lower K_{ow}, since they are more likely to partition into the organic phases. To the contrary, the average log ratios of different groups of organochlorines at a particular trophic level were very similar (Table 3). At Station 7C or 9C, the average values of $\log K_{ms}$, $\log K_{ls}$, $\log K_{ps}$ for compounds with K_{ow} between 6.00-7.36 were not significantly different (Table 3), suggesting no selective bioaccumulation and biomagnification of highly hydrophobic compounds. The only supporting evidence for biomagnification in this study were the concentrations of DDEs and DDDs in different compartments at all stations, generally in the order of liver (hornyhead turbot) > muscle (hornyhead turbot) > polychaetes > sediment (Figure 3). These increments among the various trophic levels, however, are not significant enough to confirm with certainty the presence of biomagnification. Taken together, the gathered information suggests that the accumulation of chlorinated hydrocarbons in hornyhead turbot occurred more likely through the equilibrium partition process in which its lipid content played an important role. It is possible that uptake of contaminants may also take place via the food chain transport pathway. This second route of accumulation, however, does not appear to result in a significant increase in the levels of contaminant uptake.

Hornyhead turbot are mobile animals. After the fish moves into a sampling location, an extended period of time may be required for the original level of tissue contamination to achieve an equilibrium with the ambient contaminant level (Mortimer and Connell 1996). In addition, other components such as sex, weight, and lipid content may further complicate the bioaccumulation process. These and many other environmental factors may confound field observations and obscure the underlying bioaccumulation mechanisms (Bierman 1990). Furthermore, the partitioning coefficients and bioaccumulation factors are widely distributed due to the difficulty in detecting the target analytes at low concentrations, where small errors may result in large variations. Within this perspective, correlations among the various partitioning coefficients should be viewed as possible trends rather than statistically supported facts. Nevertheless, our findings in this study reveal that historically discharged contaminants continue to be accumulated in biota, primarily through direct diffusion uptake. The evidence for biomagnification of toxic chemicals (DDEs and DDDs) should be a concern, since potential toxic effects may be induced in exposed species as well as many demersal fish occupying higher trophic levels that are taken for human consumption.

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