

Trophic Magnification of PCBs and Its Relationship to the Octanol–Water Partition Coefficient

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S Supporting Information

ABSTRACT: We investigated polychlorinated biphenyl (PCB) bioaccumulation relative to octanol–water partition coefficient (K_{OW}) and organism trophic position (TP) at the Lake Hartwell Superfund site (South Carolina). We measured PCBs (127 congeners) and stable isotopes ($\delta^{15}N$) in sediment, organic matter, phytoplankton, zooplankton, macroinvertebrates, and fish. TP, as calculated from $\delta^{15}N$, was significantly, positively related to PCB concentrations, and food web trophic magnification factors (TMFs) ranged from 1.5–6.6 among congeners. TMFs of individual congeners increased strongly with $\log K_{OW}$, as did the predictive power (r^2) of individual TP-PCB regression models used to calculate TMFs. We developed $\log K_{OW}$ -TMF models for eight food webs with vastly different environments (freshwater, marine, arctic, temperate) and species composition (cold- vs warmblooded consumers). The effect of K_{OW} on congener TMFs varied strongly across food webs (model slopes 0.0–15.0) because the range of TMFs among studies was also highly variable. We standardized TMFs within studies to mean = 0, standard deviation (SD) = 1 to normalize for scale differences and found a remarkably consistent K_{OW} effect on TMFs (no difference in model slopes among food webs). Our findings underscore the importance of hydrophobicity (as characterized by K_{OW}) in regulating bioaccumulation of recalcitrant compounds in aquatic systems, and demonstrate that relationships between chemical K_{OW} and bioaccumulation from field studies are more generalized than previously recognized.



INTRODUCTION

Persistent organic contaminants (OCs) are widespread in the environment and pose serious health risks to humans and wildlife.^{1,2} Regulatory agencies have long relied on bioconcentration factors (BCFs) or bioaccumulation factors (BAFs) to evaluate risks and manage toxic substances,³ but trophic magnification factors (TMFs) derived from stable isotope analysis are increasingly used to quantify biomagnification of OCs in the environment.⁴ TMFs, which measure the average biomagnification of contaminants through food webs, have a number of advantages over traditional BCFs and BAFs because they are not prone to uncertainty in measurement of water concentrations, they account for ecological complexity in trophic interactions, and they measure biomagnification across entire food webs rather than for individual species.^{3–6}

In spite of the widespread application of the TMF approach, challenges remain in identifying general patterns in biomagnification among ecosystems and food webs. TMFs for a given OC

can vary widely among studies depending on the types of consumers (e.g., poikilotherms or homeotherms) included in the analysis, the range of trophic levels investigated, and other factors.^{6–9} These issues arise not only when comparing the magnitude of biomagnification among systems for single contaminants, but also when investigating biomagnification related to physical/chemical properties of OCs themselves.

The *n*-octanol–water partition coefficient (K_{OW}) is a primary regulator of biomagnification of recalcitrant compounds like PCBs in aquatic food webs.^{10,11} Compound K_{OW} s are constant among different environments, although they vary slightly with temperature¹² and salinity.¹³ However, TMFs for PCBs increase sharply (up to 15 \times) with each unit increase in $\log K_{OW}$ in some

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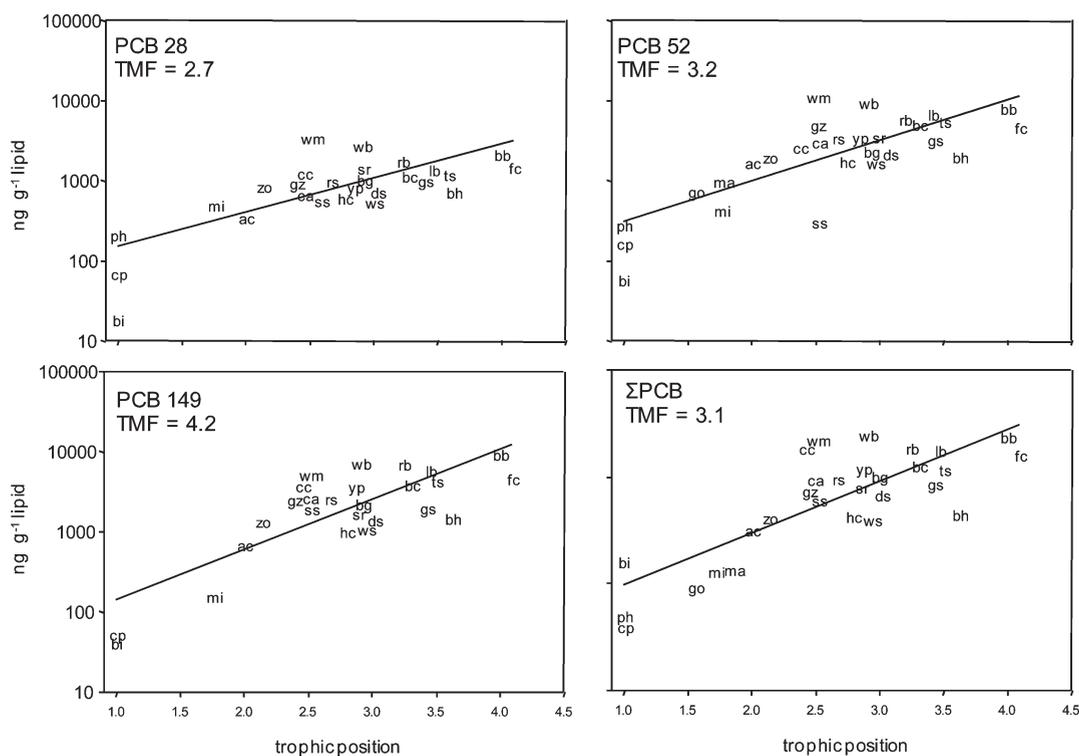


Figure 1. Relationship between trophic position (TP) and PCB concentrations (ng g^{-1} lipid) for the Lake Hartwell food web. Symbols represent mean values for each food web component. Organic matter: **bi**, biofilm; **cp**, CPOM; **ph**, phytoplankton. Invertebrates: **ac**, Asian clam; **go**, gomphidae; **ma**, *Macromia*; **mi**, midge; **zo**, zooplankton. Fish: **bb**, black buffalo; **bh**, black bullhead; **bc**, black crappie; **bg**, bluegill; **ca**, common carp; **cc**, channel catfish; **ds**, dollar sunfish; **fc**, flathead catfish; **gs**, green sunfish; **gz**, gizzard shad; **hc**, highfin carpsucker; **lb**, largemouth bass; **rb**, redbreast sunfish; **rs**, redear sunfish; **ts**, threadfin shad; **wb**, white bass; **ws**, whitefin shiner; **wm**, warmouth; **yp**, yellow perch. Parameters for regression models are provided in Table 1. Scientific names are provided in SI Table S1.

food webs but show little or no increase in others.^{9,14} It is unclear if these differences (i.e., apparent overall dependence of the TMF upon the K_{OW} of the chemical) are related to ecological differences among food webs or to methodological differences among studies.

We investigated patterns of PCB biomagnification in Lake Hartwell (South Carolina), a warm-temperate reservoir with a legacy of severe contamination.¹⁵ Our first objective was to characterize PCB biomagnification within the Lake Hartwell food web, and we expected that PCB concentrations would increase with trophic position (TP). Next, we quantified the dependence of the TMF upon the K_{OW} for PCB congeners and the predictive power (i.e., coefficient of determination, r^2) explained by TP-PCB regression models. TMFs and predictive power of TP on congener concentrations should increase with K_{OW} , except for the most hydrophobic compounds (e.g., nona- and deca-CBs), as uptake from food and loss via elimination of waste become increasingly important to biomagnification as hydrophobicity increases.^{10,11} Finally, we used an innovative approach to analyze or interpret $\log K_{OW}$ – TMF relationships from Lake Hartwell and other published studies to describe the generality of K_{OW} effects on PCB biomagnification.

EXPERIMENTAL SECTION

Study Area. Lake Hartwell was contaminated with PCBs from the Sangamo-Weston capacitor plant located on a tributary 25 km upstream of the reservoir. The plant discharged ~ 181.4 t

of PCBs, primarily Aroclors 1016, 1242, and 1254, into the aquatic environment from 1955 to 1977.¹⁵ The Twelvemile Creek arm (TCA) of Lake Hartwell (Supporting Information (SI) Figure S1) remains heavily contaminated with PCBs.^{16–18} Sediment concentrations generally range from ~ 500 – 6500 ng g^{-1} (dry weight) in the TCA,¹⁶ peaking near the top of the reservoir and then gradually declining down-lake.¹⁸ The TCA has mostly fine-grained sediments (sand, silt and clay), and macrophytes are uncommon due to fluctuating water levels, steep banks, and high turbidity.

Food Web Characterization. Detailed methods for sample collection and storage are provided in the SI. We collected samples of sediment, organic matter, zooplankton, macroinvertebrates, and fish in Lake Hartwell in 2005 and 2006 (SI Figure S1). Organic matter sources for the food web included CPOM (coarse particulate organic matter), epiphytic algae (biofilm), and phytoplankton. Zooplankton were pooled for analysis. The dominant taxa were *Keratella* sp. (Rotifera) and Diaptomidae (Calanoida, Copepoda); other abundant taxa are listed in the SI. Macroinvertebrate taxa included midges (nontanypodinae chironomids), odonates, and Asian clam (*Corbicula fluminea*) (SI Table S1). We collected 21 fish species ranging from filter feeding planktivores to piscivores (SI Table S1). Subsamples of CPOM, biofilm, phytoplankton, and zooplankton were removed for stable isotope analysis. Macroinvertebrate samples for PCB and stable isotope analysis were composites of multiple individuals. Fish were analyzed whole for PCBs, and skinless dorsal muscle tissue was analyzed for stable isotopes. Fish were analyzed individually except for

small-bodied fishes (<150 mm total length) which were composited for PCB and stable isotope analysis. Only adult fishes were sampled to avoid variation in chemical signatures that could be related to ontogenetic changes in diet.

Analysis of PCBs, Lipids, and TOC. Detailed methods for sample extraction, PCB quantification, quality control procedures, and total organic carbon (TOC) analysis are provided in the SI. Analysis for PCB congeners was by gas chromatography/mass spectrometry (GC/MS). This method quantified 118 GC peaks representing 127 congeners (SI Table S2) which were summed to calculate Σ PCBs. Approximate minimum detection limits ranged from 0.01 to 0.1 ng·g⁻¹ (wet weight, ww) among congeners. A minimum of four surrogate standards (SS), including CBs 14, 29, 34, 36, 61, 152 186, and 192, were added to samples prior to extraction. Recovery of SS was 67.3% (\pm 17.7, 1SD). Reported concentrations were not corrected for recovery efficiency because recoveries did not vary systematically among samples or among congeners used as surrogate standards. An aliquot of tissue extracts was analyzed for lipids using the gravimetric method¹⁹ and an aliquot CPOM samples was analyzed for TOC by standard methods (SI).

$\delta^{15}\text{N}$ Analysis and Trophic Position Calculations. Samples for $\delta^{15}\text{N}$ analysis were freeze-dried, milled, and homogenized. Homogenates were combusted and reduced to N₂ with a CHN analyzer (Carlo Erba NA 1500) with a continuous flow to an isotope ratio mass spectrometer (Finnigan Delta). Atmospheric N₂ was used as a $\delta^{15}\text{N}$ reference standard. Reproducibility was monitored using bovine liver (NIST No. 1577b) analyzed every 10 samples, and precision was 0.13‰ (1 SD) for $\delta^{15}\text{N}$.

Trophic position (TP) was determined following Post et al.²⁰ and Jardine et al.⁴ using the following equation:

$$\text{TP}_{\text{consumer}} = [(\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{Asian clam}})/3.4] + 2 \quad (1)$$

where $\delta^{15}\text{N}_{\text{consumer}}$ is the mean $\delta^{15}\text{N}$ of the organism, mean $\delta^{15}\text{N}_{\text{Asian clam}} = 8.46$ (0.12 SE), and 3.4 is the isotopic trophic enrichment factor (i.e., the average difference, $\Delta^{15}\text{N}$, between an animal and its diet). Long-lived primary consumers like Asian clam are typically used to establish an isotopic baseline necessary for calculating trophic position.^{4,20} The trophic position of organic matter sources was assigned a value of 1.0 to reflect their basal position in the food web.

Data Analysis. We calculated a TMF for individual congeners and Σ PCBs following Fisk et al.⁸ and Jardine et al.⁴ We used linear regression to determine the relationship between PCBs (lipid or TOC normalized depending on matrices) and TP:

$$\log_{10} \text{PCB}_{\text{lipid}} = b + (m \times \text{TP}) \quad (2)$$

The slope m of eq 2 was then used to calculate TMF:

$$\text{TMF} = 10^m \quad (3)$$

We used regression analysis to determine the effect of $\log K_{\text{OW}}$ on TMFs and the predictive power (r^2) of TP-PCB_{lipid} models. $\log K_{\text{OW}}$ values were from Hawker and Connell 1988.²¹ We excluded coeluting congeners, congeners that occurred in <50% of samples, and congeners detected in <75% of food web components (i.e., organic matter types and individual taxa). This resulted in a total of 64 congeners used in this analysis.

For comparison purposes, TMFs for a generalized lake food web were calculated from chemical residues predicted using the Arnot and Gobas²² food web model. The generalized food web consisted of phytoplankton, zooplankton, benthic invertebrates,

Table 1. Trophic Magnification Factors (TMFs) Calculated for the Lake Hartwell Food Web from Regression Models of Trophic Position (TP) Versus Log₁₀ PCB Concentrations (ng g⁻¹ lipid)^a

congener	log K_{ow}	TMF	slope	error	r^2	p
PCB 9	5.06	1.95	0.29	0.12	0.20	0.0235
PCB 17	5.25	1.94	0.29	0.12	0.20	0.0204
PCB 18	5.24	1.71	0.23	0.11	0.16	0.0431
PCB 19	5.02	1.46	0.16	0.09	0.12	0.0798
PCB 22	5.58	2.29	0.36	0.08	0.43	0.0003
PCB 25	5.67	2.23	0.35	0.10	0.35	0.0014
PCB 26	5.66	2.39	0.38	0.09	0.42	0.0003
PCB 27	5.44	1.82	0.26	0.10	0.24	0.012
PCB 28	5.67	2.68	0.43	0.07	0.58	<0.0001
PCB 31	5.67	2.65	0.42	0.08	0.51	<0.0001
PCB 32	5.44	2.25	0.35	0.13	0.25	0.0096
PCB 37	5.83	2.01	0.30	0.08	0.37	0.0011
PCB 44	5.75	2.83	0.45	0.09	0.50	<0.0001
PCB 45	5.53	2.98	0.47	0.13	0.35	0.0014
PCB 47	5.85	3.57	0.55	0.08	0.65	<0.0001
PCB 48	5.78	2.65	0.42	0.11	0.37	0.001
PCB 49	5.85	3.10	0.49	0.07	0.62	<0.0001
PCB 52	5.84	3.21	0.51	0.08	0.61	<0.0001
PCB 53	5.62	1.91	0.28	0.09	0.27	0.0053
PCB 56	6.11	2.96	0.47	0.08	0.59	<0.0001
PCB 60	6.11	3.32	0.52	0.09	0.59	<0.0001
PCB 64	5.95	3.06	0.49	0.08	0.59	<0.0001
PCB 66	6.20	3.46	0.54	0.07	0.67	<0.0001
PCB 70	6.20	3.10	0.49	0.08	0.59	<0.0001
PCB 74	6.20	3.47	0.54	0.08	0.61	<0.0001
PCB 77	6.36	2.54	0.40	0.11	0.35	0.0016
PCB 82	6.20	3.96	0.60	0.09	0.64	<0.0001
PCB 84	6.04	3.25	0.51	0.14	0.35	0.0015
PCB 87	6.29	3.52	0.55	0.09	0.60	<0.0001
PCB 91	6.13	3.60	0.56	0.09	0.62	<0.0001
PCB 92	6.35	4.30	0.63	0.10	0.63	<0.0001
PCB 95	6.13	3.10	0.49	0.08	0.62	<0.0001
PCB 97	6.29	3.72	0.57	0.09	0.62	<0.0001
PCB 99	6.39	4.06	0.61	0.09	0.64	<0.0001
PCB 100	6.23	5.07	0.71	0.13	0.56	<0.0001
PCB 101	6.38	3.48	0.54	0.08	0.66	<0.0001
PCB 105	6.65	4.01	0.60	0.10	0.59	<0.0001
PCB 110	6.48	3.26	0.51	0.07	0.65	<0.0001
PCB 118	6.74	4.10	0.61	0.09	0.65	<0.0001
PCB 124	6.73	4.87	0.69	0.12	0.56	<0.0001
PCB 128	6.74	6.00	0.78	0.15	0.52	<0.0001
PCB 130	6.80	4.99	0.70	0.13	0.53	<0.0001
PCB 134	6.55	3.90	0.59	0.12	0.50	<0.0001
PCB 135	6.64	4.65	0.67	0.13	0.53	<0.0001
PCB 136	6.22	3.96	0.60	0.12	0.50	<0.0001
PCB 137	6.83	5.89	0.77	0.14	0.57	<0.0001
PCB 138	6.83	4.20	0.62	0.11	0.58	<0.0001
PCB 141	6.82	6.18	0.79	0.15	0.54	<0.0001
PCB 144	6.67	4.28	0.63	0.11	0.56	<0.0001
PCB 146	6.89	5.01	0.70	0.10	0.65	<0.0001
PCB 149	6.67	4.18	0.62	0.09	0.65	<0.0001

Table 1. Continued

congener	log K_{OW}	TMF	slope	error	r^2	p
PCB 151	6.64	5.78	0.76	0.14	0.55	<0.0001
PCB 156	7.18	6.24	0.80	0.15	0.55	<0.0001
PCB 157	7.18	4.83	0.68	0.12	0.57	<0.0001
PCB 163	6.99	4.39	0.64	0.10	0.62	<0.0001
PCB 164	7.02	4.63	0.67	0.13	0.51	<0.0001
PCB 167	7.27	5.47	0.74	0.15	0.51	<0.0001
PCB 170	7.27	6.63	0.82	0.14	0.57	<0.0001
PCB 171	7.11	5.14	0.71	0.12	0.59	<0.0001
PCB 174	7.11	4.38	0.64	0.14	0.48	<0.0001
PCB 177	7.08	4.90	0.69	0.13	0.54	<0.0001
PCB 178	7.14	4.96	0.70	0.12	0.57	<0.0001
PCB 183	7.20	5.25	0.72	0.14	0.51	<0.0001
PCB 187	7.17	5.60	0.75	0.12	0.60	<0.0001
Σ PCB		3.09	0.49	0.07	0.68	<0.0001

^a Slope, error, r^2 , and p values are for each TP-PCB regression model. Error term is standard error of the model slope. Relationships for log K_{OW} with TMF and r^2 are shown in Figure 2.

two forage fish, and a piscivorous fish with an assumed trophic position (TP) of 1, 2, 2, 3, 3, and 4, respectively. Steady-state solutions of the Arnot and Gobas²² model were found for the log K_{OW} of each PCB congener. Equation 2 was then used to develop a linear model relating TP and predicted residues for each congener. Subsequently, eq 3 was used to determine the TMF for the congener of interest based on the slope from eq 2 (the “ m ” parameter). Details of model parametrization are provided in the SI and include diets, composition (i.e., lipid, moisture, and nonlipid matter contents), and weights of the organism.

We also compared the relationship between K_{OW} and congener TMFs for Lake Hartwell to those from other field studies reporting TMFs for PCBs across a similar range of K_{OW} s.^{8,9,14,23–25} These included food webs from marine and freshwater systems, from arctic and temperate climates, and food webs comprised entirely of homeotherms (“warm”), homeotherms and poikilotherms (“whole”), and only poikilotherms (“cold”).⁷ We used linear regression to determine relationships between K_{OW} and raw TMFs derived from these studies. The range of TMFs varied strongly among studies, so we standardized TMFs within studies to mean = 0, SD = 1 to remove scale differences in the response of TMF factors to K_{OW} among food webs. We modeled standardized TMFs using analysis of covariance (ANCOVA) with log K_{OW} as a continuous variable and individual food web studies as categorical variables.

RESULTS AND DISCUSSION

PCB Biomagnification in Lake Hartwell. Mean Σ PCBs in Lake Hartwell ranged from 30 to 16 800 ng g⁻¹ wet weight among food web components (SI Table S1). Trophic relationships derived for consumers were typical for aquatic food webs with invertebrates having lower trophic position than fishes (Figure 1). Zooplankton had the highest trophic position (TP) among invertebrates. Trophic position of fishes varied from 2.5 to 4.0 (SI Table S1), but calculated values did not always confirm expectations based on published information on adult diets.²⁶ Top predators such as piscivores (largemouth bass, *Micropterus salmoides* and flathead catfish, *Pylodictis olivaris*) had high TP values, but TP was similarly high for other planktivorous

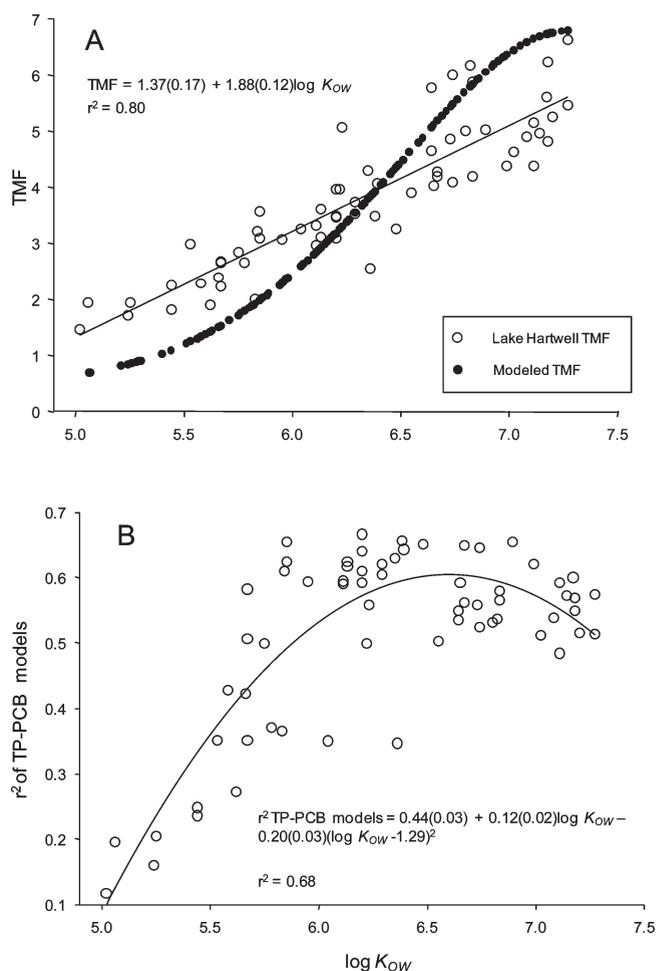


Figure 2. (A) Relationship of log K_{OW} with PCB congener TMFs for the Lake Hartwell food web and for modeled TMFs for a generalized food web.²² Regression line and equation are for Lake Hartwell data. (B) Relationship of log K_{OW} with r^2 values from regression models of TP versus log PCBs (ng g⁻¹ lipid) for Lake Hartwell. Parameters for TP – PCB models for Lake Hartwell are provided in Table 1.

(threadfin shad, *Dorosoma petenense*), omnivorous (black bullhead, *Ameiurus melas*), and invertivorous (black buffalo, *Ictiobus niger*) fish that would be expected to have lower TP values (Figure 1).

Log PCB concentrations were linearly related to TP for individual congeners and Σ PCBs (Figure 1). Much of the variation in these models can be attributed to variability among fish species. For example, total PCB_{lipid} concentrations varied 6-fold for fish with TP ~3.0, similar to variation in Σ DDT concentrations for fish in Lake Malawi, Africa.²⁷ High variation within trophic levels can be partially explained by a weakness of the TP modeling approach. Calculation of TP assumes a common fractionation rate ($\Delta^{15}N$) among consumers.⁴ However, $\Delta^{15}N$ varies widely among consumers,^{20,28} and violation of the assumption of constant $\Delta^{15}N$ causes measurement error in TP.⁴ Evidence for this type of error exists in Lake Hartwell. Black bullhead had higher TP than expected for an omnivore, and their PCB concentrations were much lower than models predicted (Figure 1). Likewise, warmouth had lower TP than expected for a generalized carnivore (consumers with a mixed diet of invertebrates and fish,²⁶), and their PCB concentrations were typically

Table 2. Linear Regression Models of Log K_{OW} Versus TMFs for Various Food Webs^a

study area	food web	citation	n	log K_{OW} vs TMF		log K_{OW} vs standardized TMF		r^2	p
				slope	intercept	slope	intercept		
Baffin Bay	whole	8	10	4.7	1.1	1.43	-9.3	0.56	0.01
Barents Sea	cold	9	9	-0.3	3.9	-0.40	2.5	0.04	0.60
Barents Sea	warm	9	9	15.4	6.2	1.59	-10.1	0.71	0.004
Beaufort-Chukchi Sea	whole	23	9	2.8	1.9	1.53	-10.0	0.72	0.004
China (reservoir)	cold	25	10	1.5	3.0	1.72	-11.0	0.72	0.002
Lake Hartwell	cold		12	1.5	2.7	1.65	-10.6	0.87	0.0001
Tokyo Bay	cold	24	8	0.4	1.2	1.64	-10.5	0.93	0.0001
White Sea	whole	14	9	0.0	1.9	0.16	-1.1	0.01	0.78

^a Data from Baffin Bay, Barents Sea, Beaufort-Chukchi Sea, and White Sea food webs were compiled by Borga et al. (ref 7 and Table 2). Models include TMFs calculated for PCBs 28, 31, 47, 52, 99, 101, 105, 118, 138, 149, 153, 180, and 194, although not all congeners were measured in each study. The same congeners were used when available for China (reservoir), Lake Hartwell, and Tokyo Bay, but other congeners with similar chlorination state were substituted as necessary to ensure that a similar range of log K_{OW} values were used among models. *N* refers to the total number of congeners used in models. Food web classifications: **cold**, food web comprised of poikilotherms (invertebrates and fish) only; **warm**, food web comprised of homeotherms (birds and mammals) only; **whole**, food web comprised of homeotherms and poikilotherms. References are for studies from which the data were compiled. Intercepts are for models that normalized K_{OW} to the lowest value ($K_{OW} = 5.56$, PCB 28). Model parameters for Lake Hartwell differ slightly from those in Figure 2A because only a subset of congeners was used for this analysis. Model r^2 and *p* values are the same for models using TMFs and standardized TMFs.

higher than predicted. Other ecological factors such as growth and elimination rates also regulate biomagnification of OCs in animals.^{29–31} These processes are largely independent of TP and could contribute unexplained variation in the TP response.

The TMFs for individual congeners ranged from 1.5 to 6.6 (Table 1). TMF was strongly, linearly related to log K_{OW} up to log K_{OW} values of ~ 7.3 ($r^2 = 0.8$, $p < 0.0001$; Figure 2A). The slope of the Lake Hartwell log K_{OW} – TMF model was 1.88, indicating that TMFs approximately doubled with each unit increase in log K_{OW} . The log K_{OW} – TMF relationship for Lake Hartwell was in good agreement with that derived from the generalized lake food web. TMFs derived from the Arnot and Gobas model demonstrated an increase in TMF with log K_{OW} , but the relationship was not linear and there were significant deviations at low and high values of K_{OW} . Trophic position (TP) explained 12–67% of the variation in PCB_{lipid} concentrations (Table 1, Figure 2B). The r^2 of TP-PCB_{lipid} models also increased significantly with log K_{OW} ($r^2 = 0.68$, $p < 0.0001$), but the relationship was nonlinear (Figure 2B).

K_{OW} is a measure of hydrophobicity and indicates partitioning potential, a fundamental property regulating biomagnification of recalcitrant OCs in the aquatic environment. The relationship between K_{OW} and PCB bioaccumulation we observed is consistent with those from modeling studies, laboratory feeding experiments, and other food web studies. Biomagnification and half-lives of recalcitrant compounds typically increase for log $K_{OW} < 7.0$, then decline due to reduced bioavailability and potentially inaccurate K_{OW} estimates for these superhydrophobic OCs.^{7,10,30,32} We found a strong linear relationship between congener TMFs and log K_{OW} in Lake Hartwell. Our criteria for developing log K_{OW} – TMF models (excluding congeners occurring in <50% of samples and congeners occurring in <75% of food web components) excluded many octo- and nona-CBs, so there is uncertainty regarding the shape of the response for higher chlorinated congeners with higher K_{OW} .

Contaminant K_{OW} not only affects biomagnification via trophic transfer but also determines the power of TP to predict contaminant concentrations. Predictive power for PCB_{lipid} models was maximized for log K_{OW} values between 5.75 and 7.0. This

curvilinear response in model r^2 is expected because the predictive power of TP should be maximized for compounds where dietary uptake and fecal egestion elimination rate are the most important processes driving exposure and bioaccumulation.³³ Model r^2 was likely lower for compounds with log $K_{OW} < 5.75$ because other processes such as bioconcentration and elimination via respiration are important for accumulation of these less hydrophobic compounds.^{7,10,22,34} Likewise, the decline in model r^2 for compounds with log $K_{OW} > 7.0$ suggest that other factors such as reduced bioavailability and slow absorbance rates lessen the role of trophic transfer in bioaccumulation of these compounds.^{10,32,33} A similar relationship could be expected for other recalcitrant OCs, but not for metabolizable high K_{OW} compounds (e.g., PAHs, PDBEs, PFOS) that demonstrate little biomagnification in aquatic food webs.^{6,24,25,35}

The two large negative residuals in Figure 2B were for PCB 77 and 84, indicating that TP-PCB models had lower r^2 than expected based on log K_{OW} (see Table 1 for model parameters). The TP-PCB_{lipid} model for PCB 77 also had a lower slope than other tetra-CBs with similar log K_{OW} values (Table 2). PCB 77 is coplanar and non-ortho substituted, and our results support previous findings that congeners with this molecular structure^{32,36} and PCB 77 in particular^{37,38} are biotransformed in aquatic food webs. PCB 84 is a chiral congener that is enantioselectively metabolized in mammals.³⁹ PCB 84 was detected in invertebrates in Twelvemile Creek (the stream delivering PCBs to Lake Hartwell) but not fish, suggesting that fish are able to metabolize PCB 84.⁴⁰ We detected PCB 84 in 92% of fish samples from Lake Hartwell, but concentrations were ~ 2 – 5 fold lower than other penta-CBs (data not shown). Concentrations among fishes were highly variable and did not follow expected trophic relationships based on $\delta^{15}N$. These results also suggest that metabolism by fish may disrupt food web bioaccumulation of PCB 84.

K_{OW} Effects on TMFs: Cross-system Comparisons. The relationship between K_{OW} and congener TMFs varied among food webs (Figure 3A). Log K_{OW} was highly predictive ($r^2 = 0.71$ – 0.85) of TMFs in all but two food webs (Barents Sea cold, $r^2 = 0.04$; White Sea whole, $r^2 = 0.01$; Figure 3A, Table 2). Model slopes were highly variable; TMFs increased from 0 – $15\times$ among

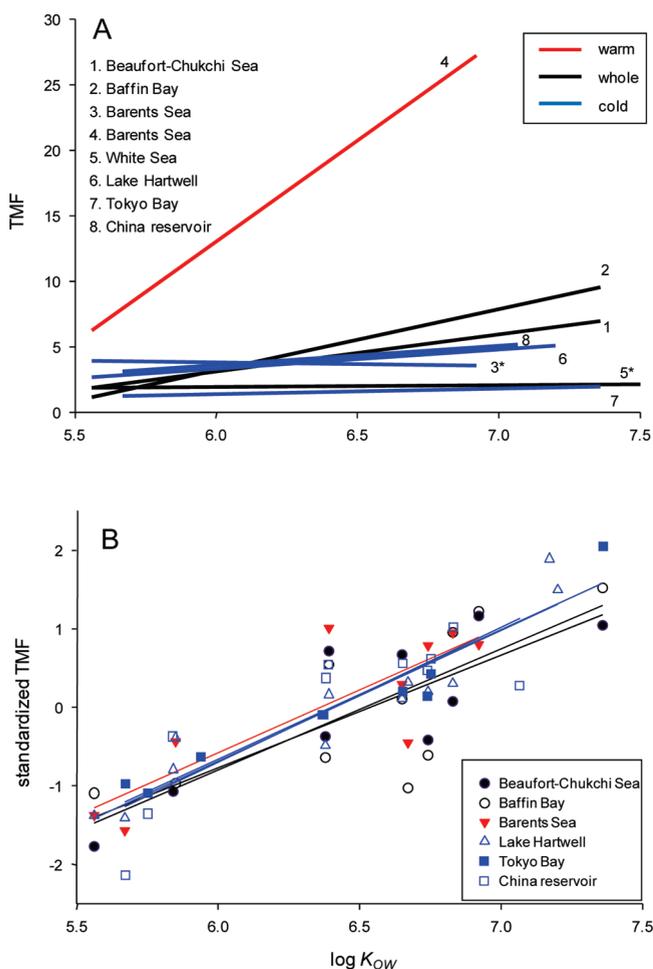


Figure 3. Effect of log K_{OW} on raw (A) and standardized (B) TMFs for various PCB congeners. Asterisks in A indicate nonsignificant models, and these studies were excluded from ANCOVA (panel B). Regression lines in B are for individual cold, whole, and warm food webs. Food web classifications: **cold**, poikilotherms only; **warm**, homeotherms only; **whole**, homeotherms + poikilotherms. Data from: Beaufort-Chukchi Sea;²³ Baffin Bay;⁸ Barents Sea;⁹ White Sea;¹⁴ Tokyo Bay;²⁴ China reservoir.²⁵

food webs for each unit increase in log K_{OW} . The greatest increase was for a warm food web, followed by whole food webs. Model slopes were lowest for cold food webs except for the White Sea whole food web, where K_{OW} had no effect. Variation in model slopes largely reflected variation in the range of TMFs among food webs (e.g., Barents Sea warm, TMFs = 5.4 – 28.4; Lake Hartwell, TMFs = 2.6 – 4.2). The K_{OW} effect on standardized TMFs was consistent among food webs (Figure 3B). Log K_{OW} was strongly linearly related with TMF (ANCOVA, full model: $F_{11, 57} = 12.6$, $r^2 = 0.75$, $p < 0.0001$; log K_{OW} : $F_{1, 57} = 134.1$, $p = < 0.0001$) and regression slopes did not differ among food webs (model slopes = 1.43–1.72, log $K_{OW} \times$ food web: $F_{5, 57} = 0.09$; $p = 0.99$). Mean slope for the whole model was 1.60 (± 0.14 SE) across food webs indicating that each unit increase in log K_{OW} resulted in a 1.6 \times increase in the mean of the standardized TMF.

Because contaminant K_{OW} s are relatively constant in the environment, it was reasonable to expect that TMF dependence on K_{OW} should be similar among food webs. However, the magnitude of the TMF response had not previously been compared among food webs. Comparisons are problematic due to

ecological differences among food webs and methodological differences among studies. Regression models using raw TMFs indicated that food web type strongly affected the magnitude of the log K_{OW} response. Regression slopes were steepest in a warm food web, intermediate in whole food webs, lowest in cold food webs, and nonsignificant for two food webs. Standardized TMFs demonstrated a consistent response (1.6 \times increase with each unit increase in log K_{OW}) among those food webs with a significant K_{OW} effect. This generalized finding underscores the importance of hydrophobicity in regulating biomagnification of recalcitrant compounds in the environment.

TMF Application. Comparing TMFs across systems has yielded insight into important processes (e.g., comparing exposure at the base of the food web by comparing intercepts of the regressions,⁷), yet comparisons are challenging due to ecological differences among food webs and methodological differences among studies. For example, TMFs are typically higher in food webs having consumers with high lipid content, warm-blooded apex predators, and longer food chains.^{7,8,37} However, some differences in TMFs could result from different methodologies, such as the inclusion of basal organic matter when analyzing TP-PCB relationships (ref 41, this study). Comparisons of TMFs among studies would benefit from an approach similar to the one that we used to compare K_{OW} effects among studies. That is, standardize TP and contaminant concentrations to their mean and variance within studies to remove scale differences among studies prior to making comparisons.

TMFs provide solid empirical evidence of biomagnification in the field, yet integrating TMF information into regulatory and risk management decision-making is an ongoing challenge.³ Currently, regulatory agencies assess bioaccumulation potential based on a chemical's K_{OW} and bioconcentration factor (BCF). Gobas et al.⁴² recently proposed a chemical assessment framework giving preference to TMF and BMF data over BCF and K_{OW} since the TMF and BMF provide insights regarding the potential for a substance to biomagnify. This framework brings field measurements that are currently ignored into the assessment process. By including TMFs and BMFs in the framework, decisions on a chemical's bioaccumulation potential can be based upon a much broader range of bioaccumulation data (lab and field) and will help to prevent or reduce the miscategorization of individual chemicals.

TMFs measure biomagnification of chemicals within food webs; however, TMFs do not capture the bioaccumulation of chemicals from sediment and water to organisms in the food web. Use of TMFs to predict bioaccumulation will require the development of methods for establishing the relationship between the sediment and water to the base of the food web. Two approaches are available for establishing these relationships. First, direct measurement of the sediment, water, and base of the food web could be done in the ecosystem where the TMF was determined. Second, mechanistic food web models^{22,43} could be used to model and predict these relationships. These methods, in combination with the TMF, would enable prediction of chemical residues in organisms within a specific food web. Investigations into the underlying behavior of TMFs are important for acceptance of TMFs into regulatory and risk management decision-making processes. This report demonstrates that TMFs are well-behaved with respect to the chemical's hydrophobicity (expressed using K_{OW}) and that predictions from mechanistic bioaccumulation models are consistent with field observations.

■ ASSOCIATED CONTENT

Supporting Information. Sample collection, analytical methods for PCBs and TOC; modeling TMFs for a generalized food web; characterization of fish trophic guilds; data for ΣPCBs, lipids, TOC, and TP; list of PCBs analyzed; and study area map. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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