Influence of Trophic Position and Spatial Location on Polychlorinated Biphenyl (PCB) Bioaccumulation in a Stream Food Web

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We tested the ability of δ^{15}N-derived trophic position (TP) to predict polychlorinated biphenyl (PCB) concentrations in a historically contaminated stream (Twelvemile Creek, SC). We analyzed sediment, four types of organic matter, 27 macroinvertebrate taxa, and 25 fish species from six sites spanning 25 stream km. ΣPCBs were high across sites (mean fish = 2505 ng g^{-1} wet), with little spatial variation in concentrations within a trophic level. ΣPCBs (wet weight) were significantly positively correlated with TP ($r^2 = 0.56$) and lipids ($r^2 = 0.44$), and concentrations increased 1–2 orders of magnitude among trophic levels. After adjusting for lipids, we calculated a food web magnification factor of 1.6 for ΣPCBs, which is low compared to marine and lentic food webs. The predictive power of TP for individual congeners increased with K_{ow} (octanol–water partition coefficient), with regression slope ~ 0.48 and $r^2 \sim 0.70$ for $K_{ow} > 6.5$. The proportion of high K_{ow} compounds increased with distance from the source and with trophic position. Spatial variation in congener patterns was high, in contrast to marine and lentic systems where variation is typically low.

Introduction

Bioaccumulation of persistent organic contaminants (OCs) is well documented in lentic and marine ecosystems (*1, 2*), but few studies have addressed OC bioaccumulation in streams (e.g., refs *3–6)*. The limited research in streams is surprising given the magnitude and extent of OC pollution. Approximately 9% of wadeable stream length in the U.S. is underlain by contaminated sediments including OCs (*7*); atmospheric deposition of OCs into streams is widespread (*3*), and OCs in stream fishes often exceed wildlife risk values, even in remote locations (*4*). Human health risks from consumption of lotic fishes are widespread, with 38% of U.S. stream length listed as "impaired" for fish consumption, primarily due to bioaccumulative compounds such as polychlorinated biphenyls (PCBs) (*8*).

Ratios of stable nitrogen isotopes, $^{15}N/^{14}N$ or $\delta^{15}N$, are increasingly used to assess dietary exposure of OCs in aquatic food webs (*2, 9*). $\delta^{15}N$ is a strong predictor of OCs in aquatic food webs (*2, 10*), but recent studies advocate the use of δ^{15}N-derived values of trophic position (TP) to assess bioaccumulation (*9, 11*). TP values account for spatial variation in baseline $\delta^{15}N$ of the environment and facilitate among-site comparisons of OC biomagnification (*12*). $\delta^{15}N$ has been used sparingly to assess trophic structure and bioaccumulation among trophic levels in streams (*13, 14*), but neither TP nor $\delta^{15}N$ have been used as predictors of OCs in stream food webs. Studies of stream OC bioaccumulation have relied on limited samples of a few targeted species (e.g., refs *3*, *6*, *13*, *14*), and none have addressed TP effects on bioaccumulation across the breadth of stream organic matter sources and consumers.

We investigated patterns of OC bioaccumulation in a stream with a legacy of severe PCB contamination. The Sangamo-Weston capacitor plant (Pickens, South Carolina) operated from 1955 to 1977 and discharged 181.4 MT of PCBs into Twelvemile Creek (*15*). Monitoring subsequent to mitigation (soil incineration and groundwater treatment) focused on stream sediments and in situ deployments of Asian clams (*Corbicula fluminea*), but PCBs in the stream food web were not measured. Our first objective was to quantify the extent and magnitude of PCB contamination to assess the dynamics of stream recovery from contamination. For example, high levels of PCBs throughout Twelvemile Creek would indicate either ongoing inputs from the source, or in-stream retention of legacy inputs. Conversely, a pattern of increasing PCBs downstream would indicate downstream export of contaminated sediments. Our second and primary objective was to assess the utility of TP to predict OC concentrations in stream food webs and to compare our findings with those from marine and lentic systems. Our final objective was to assess trophic and spatial patterns in PCB congener composition. The proportion of high K_{ow} (octanol–water partition coefficient) congeners increases with trophic level in aquatic food webs including streams (*5, 16–18*). Congener composition in streams varies over small distances (*3, 5, 19*), whereas spatial variation in marine and lentic systems is low over vast areas (*1, 20*). Few studies have addressed both spatial and trophic variation in congener patterns (e.g., ref *5*), and comparisons between streams and other aquatic systems are generally lacking.

Experimental Section

Sample Collection. We sampled six sites from 0 to 25 km downstream of the Sangamo-Weston site (Figure 1). Sites were sampled in May and November, 2003 and 2004. Four sites were sampled both seasons and two (sites 4 and 5) were sampled only in May. An upstream reference site was sampled both seasons in 2004. Sites ranged from 8 to 35 m wide, and varied from high-gradient, bedrock sites to low-gradient, sandy sites. Three replicate samples of each matrix (i.e., organic matter and consumers) were collected for $\delta^{15}N$ analysis, and one sample was collected for PCB analysis at each site and sampling event. A list of consumers is provided in Supporting Information Table S1. Sediment was analyzed for PCBs, but not for $\delta^{15}N$. Collection methods of conditioned leaves (i.e., coarse particulate organic matter, CPOM), seston, fine benthic organic matter (FBOM), biofilm, macroinvertebrates, and fishes for chemical analyses are provided in Walters et al. (*21*). Surface sediment (0–3 cm) was collected from multiple depositional areas throughout each site using a metal scoop (*22*).

All macroinvertebrates were analyzed whole for $\delta^{15}N$ and PCBs except crayfish $\delta^{15}N$ was measured using tail muscle

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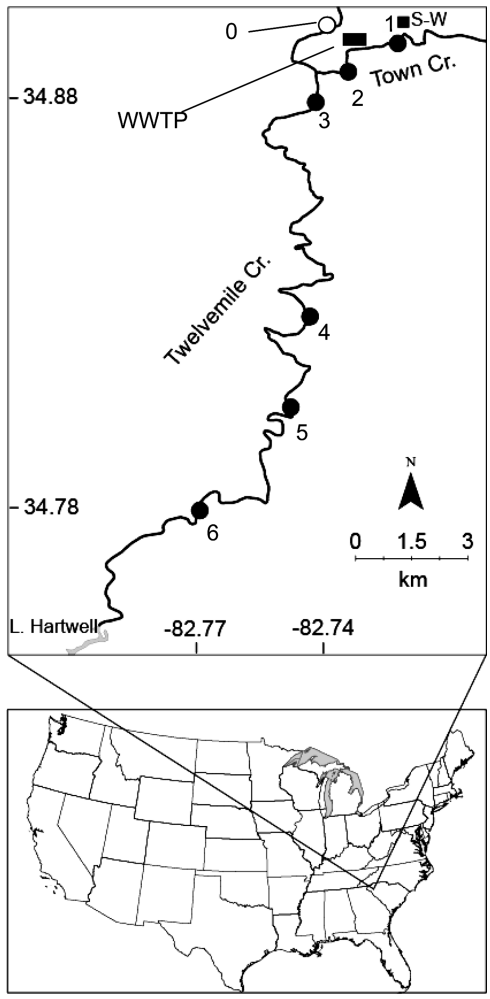

FIGURE 1. Sample sites in Twelvemile Creek (reference site, open circle). S-W = Sangamo-Weston site; WWTP = wastewater treatment plant.

tissue. Fishes were analyzed whole for PCBs, and skinless dorsal muscle tissue was analyzed for δ^{15}N. Samples were usually composites of several individuals of a similar size (e.g., <10% variation in length for fish) to minimize within-population variance.

Consumers were categorized into trophic guilds to facilitate calculation of trophic position and for ordination analyses of congener patterns. Macroinvertebrates were assigned to shredder, grazer, collector−gatherer, collector–filterer, omnivore, and predator guilds (Supporting Information Table S1) based on functional feeding groups and diet summaries provided by Merritt and Cummins (*23*). Fish were assigned to omnivore, insectivore, and generalized carnivore guilds using regional texts (e.g., ref *24*).

δ^{15}N Analysis and Trophic Position Calculations. Samples were freeze-dried and then ground to a fine powder using a ball mill. Samples were combusted to N_2 and analyzed in a Carlo Erba NA 1500 CHN analyzer connected to a Finnigan Delta C isotope ratio mass spectrometer. Isotope values were expressed as δ^{15}N (‰) according to the following equation:

$$\delta^{15}\mathrm{N} = [(R_{\mathrm{sample}}/R_{\mathrm{standard}} - 1)] \times 1000 \quad (1)$$

where $R = {}^{15}\mathrm{N}/{}^{14}\mathrm{N}$. The reference standard for δ^{15}N was atmospheric N_2. Reproducibility was monitored using bovine liver (NIST no. 1577b) analyzed every 10 samples, and precision among these standard samples was better than 0.2‰ (1 SD).

Trophic position (TP) was calculated for each site following Cabana and Rasmussen (*12*) using the following equation:

$$\mathrm{TP}_{\mathrm{consumer}} = [(\delta^{15}\mathrm{N}_{\mathrm{consumer}} - \delta^{15}\mathrm{N}_{\mathrm{primary\ consumer}})]/3.4 + 2 \quad (2)$$

where $\delta^{15}\mathrm{N}_{\mathrm{primary\ consumer}}$ is the mean δ^{15}N calculated for all grazing and shredding macroinvertebrates and 3.4 is the isotopic trophic enrichment factor, or the average difference in δ^{15}N between and animal and its diet (*25*). Site means for consumers were calculated using all replicate samples from all sampling events. Methods for baseline correction in marine and lentic systems are well established and usually depend upon long-lived primary consumers such as mussels (e.g., refs *12*, *25*). These techniques are less well developed in streams, due in part to the scarcity of long-lived, ubiquitous primary consumers (*9*). We used grazers and shredders (Supporting Information Table S1) for baseline correction since they consume biofilm and CPOM (respectively), the main organic matter sources to stream food webs, and because multiple taxa from each group were collected at all sites.

Analysis of PCBs, Lipids, And Total Organic Carbon (TOC). Organic matter and consumers were analyzed for 20 PCB congeners (Supporting Information Table S1). CPOM, macroinvertebrates, and fishes were homogenized, mixed with anhydrous Na_2SO_4, and extracted in a Dionex ASE-200 using a combination of either methylene chloride and hexane or acetone and hexane. The extract was eluted through an alumina-N (level III) column with hexane, then cleaned with sulfuric acid. Analysis was by gas chromatography-electron capture detection (GC-ECD, Agilent 6890). Detection limits (DL) were 0.65–10 ng g^{-1} for sample mass ranging from 8 to 0.5 g. Only 10% of samples weighed <0.5g, and PCBs were always >DL in these samples (mean ΣPCB = 845 ng g^{-1} wet). Analytes not detected in a sample were assigned a 0 value. Reagent blanks were run twice per batch (19 samples) and were always <3 times the DL. Laboratory fortified blanks (LFBs) were analyzed twice per batch to assess recovery and reproducibility (the relative percent difference (RPD) between the two LFBs). Recovery averaged 97% (±18% SD), and RPD averaged 11% (±15% SD). Lipids in CPOM, biofilm, and consumers were measured with the graviometric method, and TOC in sediment, FBOM, and seston was measured using EPA SW-846 Method 9060A.

Data Analysis. Among-site differences in ΣPCBs were tested for four groups of matrices: (1) sediment, FBOM, and seston; (2) CPOM and biofilm; (3) macroinvertebrates and (4) fishes. Samples from all sampling events were included in this analysis to achieve adequate samples sizes. Sediment, seston, and FBOM were pooled since they represent both deposited and suspended sediment and associated organic matter. CPOM and biofilm were pooled because they are the primary basal resources of stream food webs. Macroinvertebrates and fish were pooled into consumer categories because individual trophic guilds were inadequately represented to allow for among site comparisons. Some trophic guilds (e.g., insectivores) had suitable sample numbers, and spatial patterns for these groups mirrored those for pooled consumer categories. All odonates were excluded from this and subsequent analyses because PCBs in these predators were consistently very low (often below detection limits, see Supporting Information Table S1) relative to other macroinvertebrates.

Among-site differences in ΣPCB were determined by Analysis of Covariance (ANCOVA, SYSTAT 11) using $\log_{10}$ transformed data. Concentrations were adjusted for covariate lipid or TOC following Hebert and Keenleyside (*26*). First, we tested for significant differences between slopes of the regression lines for each site (ANCOVA interaction term).

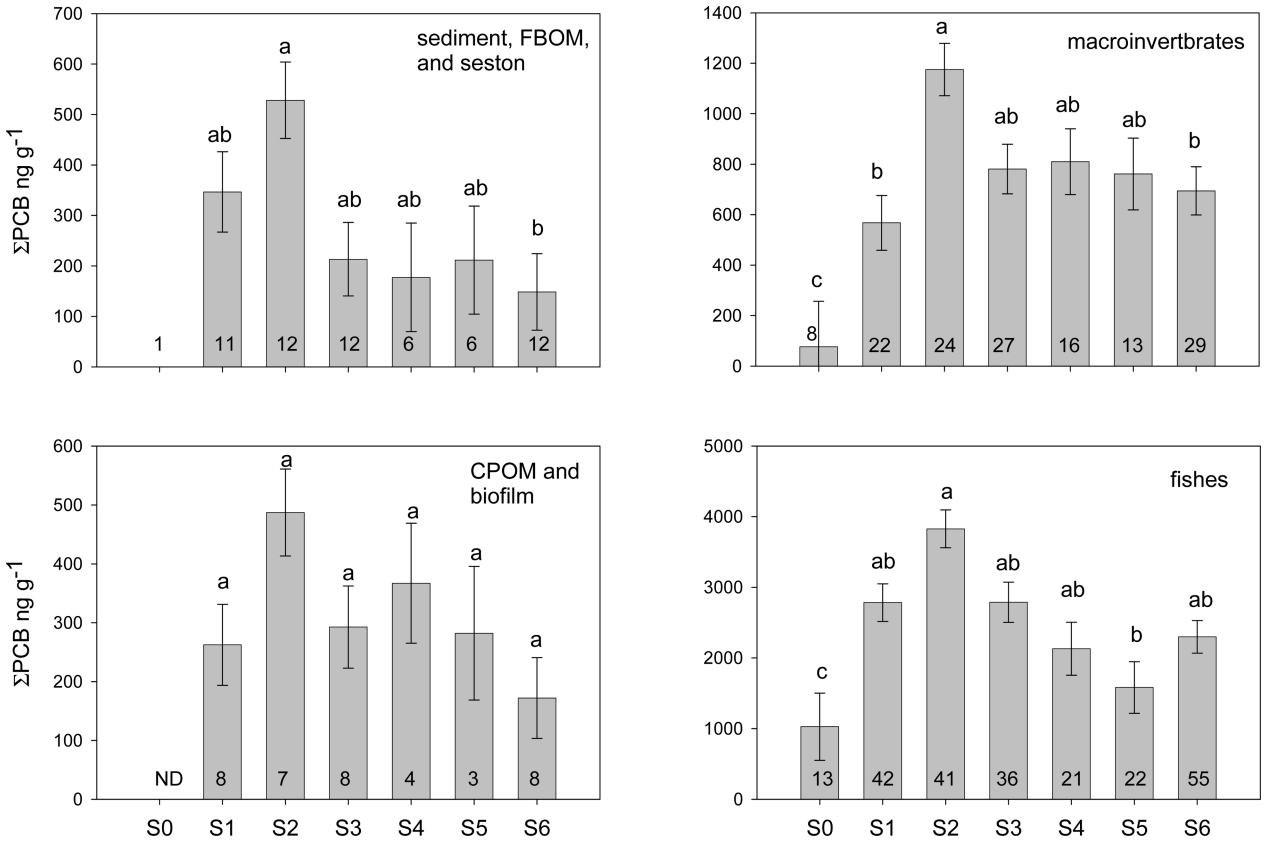

FIGURE 2. Mean among-site differences in ΣPCBs (±SE) for different trophic levels (note different scales for ΣPCB concentration in each compartment). Means were lipid/TOC adjusted using ANCOVA (see methods). Numbers within bars indicate sample size. Site numbers are on the *x*-axis. Sites with different letters are significantly different (α = 0.05, posthoc Tukey test). ND: not determined.

Interaction terms were not significant, so we used the common slope to adjust for lipid and TOC. Among-site differences in adjusted means were assessed using a posthoc Tukey test.

We used simple and stepwise multiple linear regression (JMP 5.0, SAS Institute) to assess the effect of lipids and TP on ΣPCBs. Percent lipid and ΣPCB were $\log_{10}$ transformed prior to analysis. Samples below the detection limit were dropped from analysis (e.g., ref *11*). FBOM and seston were excluded from lipid analyses since these were normalized on a TOC-basis. Means for organic matter and consumers were calculated for each site by pooling observations across sampling events and then calculating a grand mean among sites. Means for organic matter and consumer taxa were determined by first calculating a mean among sampling events for each site. These were averaged among sites to calculate a grand mean. Data from all sites were included because the ANCOVA showed that among-site variation in ΣPCB was low compared with trophic level variation. Site 2 had higher concentrations, on average, but inclusion of these data did not alter results of regression analyses. We calculated a food web magnification factor (FWMF) following Fisk (*11*) and Jardine (*9*). We used linear regression to determine the relationship between ΣPCBs and TP:

$$\log \sum \mathrm{PCB}_{\text{lipid adjusted}} = b + (m \times \mathrm{TP}) \quad (3)$$

Lipids were adjusted using residuals from the regression model of log ΣPCBs versus log lipid (*26*). The slope m of eq 3 was used to calculate FWMF using

$$\mathrm{FWMF} = 10^{m} \quad (4)$$

We identified patterns in congener composition using nonmetric multidimensional scaling (NMS, PC-ORD 4.0, MjM Software), an indirect gradient analysis for non-normal ecological data (*27*). NMS analysis was based on trophic guilds rather than individual taxa to ensure adequate representation among sites and to simplify presentation and interpretation of results. The relative abundance of congeners was calculated for each sample. Then the mean relative abundance for each matrix (sediment, organic matter, and guild) at each site was calculated among all sampling events. Proportions were arcsine, square root transformed prior to analysis (*27*). Congener 209 was excluded because it was rarely detected (two samples).

Results and Discussion

Extent and Magnitude of Contamination. TOC and lipid effects were significant for all food web compartments ($p <$ 0.03 among tests). After adjusting for these effects, ΣPCBs in sediment, FBOM, and seston, macroinvertebrates, and fishes were significantly different among sites, but no differences were observed in CPOM and biofilm (Figure 2). Site 2 consistently had the highest ΣPCBs among food web compartments, but this difference was seldom significant (Tukey posthoc tests, Figure 2) compared with other contaminated sites downstream of the Sangamo-Weston site (SWS). PCB levels were high at all sites and trophic levels. Macroinvertebrate concentrations were about an order of magnitude higher than those at the reference site, and 55% of fishes exceeded 2000 ng g^{-1} (wet weight, whole body composites), the federally specified level for fish consumption (*15*). Fish ΣPCBs were mostly low at the reference site (~40 ng g^{-1}), but three samples exceeded 2000 ng g^{-1}. These sporadic high values suggest dispersal of fishes from downstream contaminated reaches.

High levels of PCBs throughout Twelvemile Creek indicate ongoing inputs at the SWS. If this source had been eliminated,

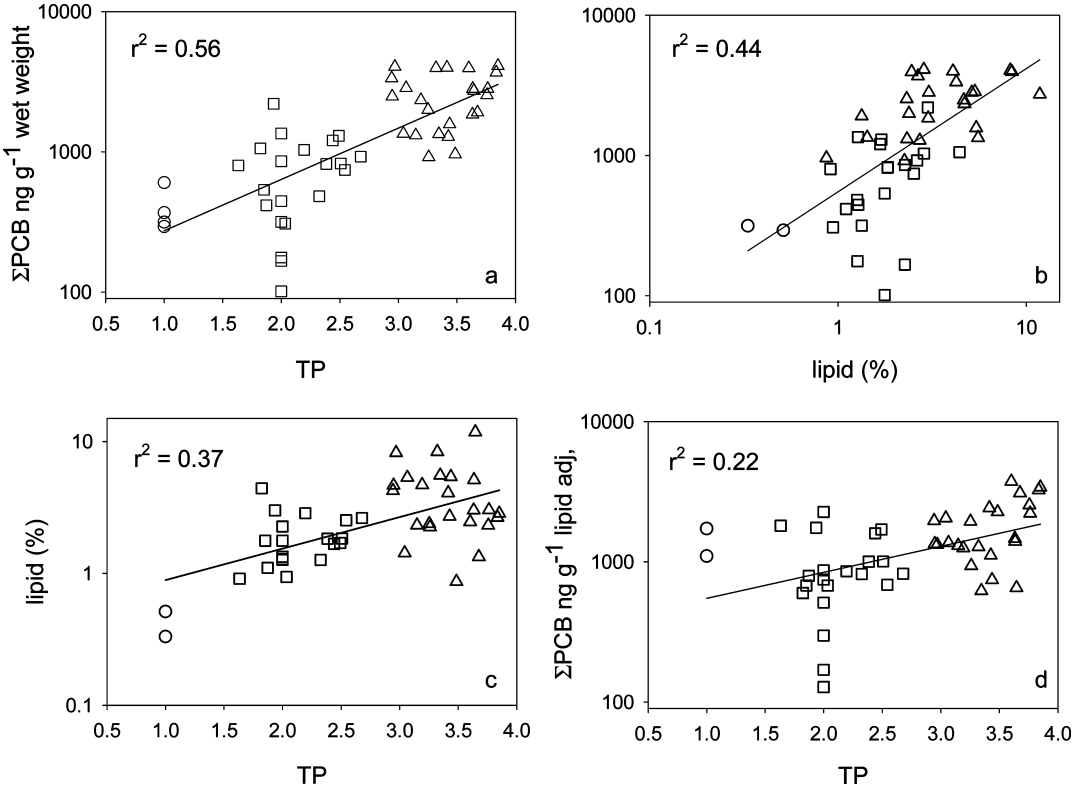

FIGURE 3. Relationships of (a) logΣPCB vs TP (logΣPCB = 2.07(0.13) + 0.37(0.05)TP); (b) logΣPCB vs lipid (logΣPCB = 2.74(0.07) + 0.88(0.15)log lipid); (c) lipid vs TP (log lipid = −0.29(0.13) + 0.24(0.05)TP); (d) logΣPCB$_{\text{lipid adjusted}}$ vs TP (logΣPCB = −0.51(0.15) + 0.19(0.05)TP). $p < 0.0008$ for all models. Circles: organic matter; squares: macroinvertebrates; triangles: fishes.

we would have expected either low levels throughout Twelvemile Creek or increasing levels downstream as contaminated sediment is exported from the system. PCBs in sediment at site 1 are dominated by low K_{OW} compounds, similar to those of a 4:1 mixture of Arochlor 1069 and 1254 released from the SWS (*28*). This suggests that PCBs near the plant have undergone little weathering (environmentally mediated changes in congener distributions), supporting our conclusion of ongoing inputs from the source. This was subsequently confirmed by a 2004 study using in situ deployments of Asian clams (Craig Zeller, U.S. Environmental Protection Agency, personal communication). Site 2 had the highest ΣPCBs and is located ~1 km downstream of an abandoned wastewater treatment facility. It is possible that this facility was contaminated with PCBs from the SWS and is an additional source of PCBs to the stream.

Bioaccumulation of PCBs in the Stream Food Web. Trophic position (TP) and lipids were significantly correlated with ΣPCBs, but TP was the stronger predictor explaining 56% of the variation compared with 44% for lipids (Figure 3a and b). Lipid and TP were significantly positively correlated ($r^2 = 0.34$; Figure 3c) but both were more strongly correlated with ΣPCBs than with one another. The relationship between TP and lipid-adjusted ΣPCBs was also significant but weak ($r^2 = 0.22$, $p = 0.0008$, Figure 3d) compared with PCBs on a wet-weight basis. Stepwise regression indicated that TP was the primary predictor of ΣPCBs. The full model explained 62% of the variance in ΣPCBs with TP and lipids explaining 56 and 6% of the variance, respectively.

Lipids and trophic position (or δ^{15}N) are often collinear, so it is difficult to determine their relative importance in bioaccumulation of OCs in food webs (*10, 29, 30*). We found that TP was a stronger predictor than lipid (Figure 3a and b) and explained significant variance in lipid-adjusted ΣPCBs (Figure 3d). Regardless of the relative importance of TP and lipids in determining OC concentrations, our results demonstrate that TP is a useful predictor of OCs in stream food webs and that TP can form the basis of cross-system comparisons of bioaccumulation similar to those for marine (*1*) and lentic (*2*) ecosystems. Strong relationships with TP and PCBs were evident when the entire food web was considered. Within the major consumer groups of macroinvertebrates and fishes, TP and ΣPCBs relationships are weaker (Figure 3a and d).

We developed linear regression models for TP and individual congeners (log wet weight) to determine if predictive power of TP varied with K_{ow}. Increasing predictive power with K_{ow} is expected since TP is diet-based and biomagnification from diet increases with K_{ow} (*1, 31*). Log K_{ow} was strongly positively correlated with regression slopes ($r^2 = 0.92$) and r^2 values ($r^2 = 0.90$), and both factors were invariant at log $K_{ow} > 6.5$ (slopes ~0.48 and $r^2 \sim 0.70$, Figure 4). Similar results have been reported for lentic (*18*) and marine (*1*) food webs and for controlled feeding experiments (*32*). Fisk et al. (*32*) reported that biomagnification factors were maximized for K_{ow} of 6.5–7.0 and then declined at higher K_{ow} (presumably due to reduced bioavailability and greater elimination by feces). Slopes and r^2 of TP-CB models were asymptotic at $K_{ow} > 6.5$ and CBs with $K_{ow} > 7.0$ were either present in low concentrations (e.g., no. 170) or undetected (e.g., no. 209). These strong relationships for OCs with K_{ow} of 6.5–7.0 (i.e., model $r^2 \sim 0.70$) further underscore the utility of TP as a predictor of OC exposure in stream ecosystems.

We calculated a food web magnification factor (FWMF) of 1.6, which is low compared with published values for marine and lentic systems. Borga et al. (*1*) reported FWMFs for ΣPCBs ranging from 1.5 to 6.2 for marine food webs, and Kidd (*2*) calculated FWMFs of 4.2 and 4.4 for Lake Ontario and Lake Baikal, respectively. These marine and lentic food chains included apex predators (≥3° consumers) and were longer than the Twelvemile Creek food web where most fish predators were invertivores. Longer food chains would be

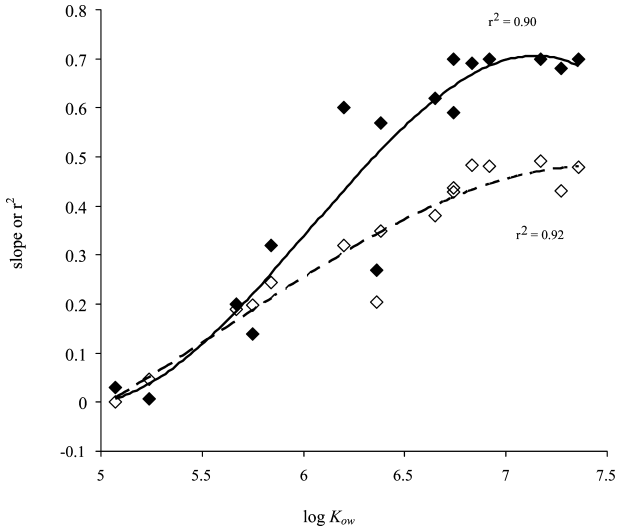

FIGURE 4. Relationship between log K_{ow} and the slope (open symbols, dashed line) and r^2 (solid symbols and line) from regression models of TP versus log CBs (wet weight) in the Twelvemile Creek food web. Modeled congeners were detected in a majority (67%) of matrixes and included congeners 8, 18, 28, 44, 52, 66, 77, 101, 105, 118, 128, 138, 153, 170, 180, and 187. Log K_{ow}values are from ref *39*.

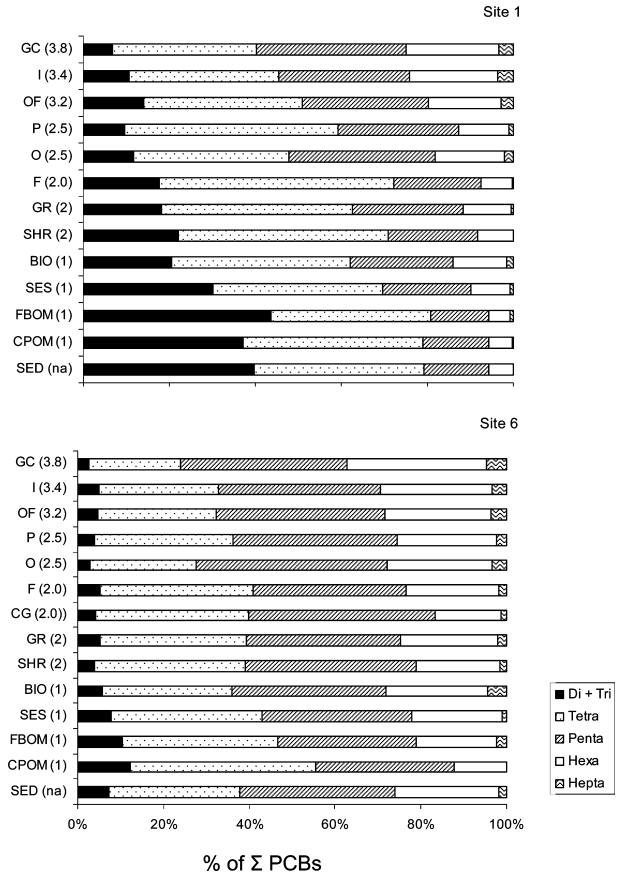

FIGURE 5. Proportion (of ΣPCB) of homologues measured at sites 1 and 6. Octa-, nona-, and decaCBs accounted for <0.1% of ΣPCBs in any group and were excluded. Numbers in parentheses indicate TP of each guild. TP was arbitrarily set at 1 for organic matter, at 2 for grazers and shredders, and was not assigned (na) for sediment. Guild information is provided in Supporting Information Table S1. Sed**, sediment;** cpom**, coarse particulate organic matter;** fbom**, fine benthic organic matter;** ses**, seston;** bio**, biofilm; macroinvertebrates:** shr**, shredder;** gr**, grazer;** cg**, collector–gatherer;** f**, collector–filterer;** o**, omnivore;** p**, predator; fishes:** of**, omnivore fish;** i**, insectivore;** gc**, generalized carnivore.**

expected to have greater slope in TP-OC regressions, and hence, higher FWMF. Our samples did not include homeotherms, and their inclusion elevates FWMFs in marine systems (*1, 11*). In addition, larger, older, lipid-rich species often have elevated concentrations of OCs (*1, 33*). Fishes in Twelvemile Creek were mostly small-bodied (<10 cm), short-lived species (2–3 y) with low lipid content compared with fishes in marine and lentic systems. Northern hogsuckers (*Hypentelium nigricans*) were the largest and oldest species we analyzed (maximum size 330 mm, lifespan 11 y (*24*)) and had the highest ΣPCBs (mean = 188 000 ng g^{-1} lipid). Thus, stream food webs with more large-bodied, long-lived species will likely have higher FWMFs than we observed.

PCB Congener Patterns. NMS analysis identified a consistent pattern of increasing higher chlorinated congeners (HCCs) with downstream distance from the SWS and with increasing trophic level (Supporting Information Figure S1). To illustrate these main effects, we calculated the mean proportion of different chlorination groups (di- + tri-, tetra-, pent-, hexa-, and heptaCBs) for all matrices collected at sites 1 (0 km from SWS) and site 6 (25 km from SWS, Figure 5). Octa-, nona-, and decaCBs comprised >0.01% of ΣPCBs in all cases and were excluded from analysis. Di- + tri and tetraCBs (lower chlorination congeners, LCCs) were more prominent at site 1 than site 6. For example, sediment and organic matter at site 1 contain 62–80% LCCs compared with only 36–56% at site 6. HCCs showed the inverse trend, increasing in sediment and organic matter from 19 to 37% at site 1 to 45–64% at site 6. HCCs within a site also increased with trophic position as reported for other aquatic food webs (*16–18*). This pattern is commonly attributed to the increasing importance of dietary intake (compared with respiration) as K_{ow} increases (*16, 31*).

Downstream increases in HCCs may be a common attribute of stream ecosystems. Farley et al. (*28*) reported similar results for sediment in the Twelvemile Creek system due to downstream loss of LCCs via volatilization. HCCs also increase downstream in fishes of the Delaware and Hudson rivers (*19*) and American Dipper (*Cinclus mexicanus*) in British Columbia streams (*3*). These consistent patterns among disparate lotic systems, ecoregions, and climatic regimes support the conclusion of Morrissey et al. (*3*) that OC uptake and retention in lotic systems is nonuniform and that consumers in larger, downstream parts of river networks are exposed to more persistent (i.e., higher K_{ow}) compounds.

Quantifying trophic variation in OC composition in streams is confounded by high spatial variation in OC composition. Compositional patterns in streams exhibit high variation at small spatial scales (10 of linear km), both from atmospheric (*3*) or industrial point sources (this study). In contrast, marine and large lentic systems have limited inputs from industrial point sources (*1*), and the composition of OCs within a trophic level are homogeneous over vast areas (*20, 34*). Spatial variation in congener profiles among sites was similar to or exceeded trophic variation assessed over just 25 stream km in this study. Consequently, studies on differential accumulation of OCs in stream food webs should account for spatial variation to better isolate trophic effects.

Unique Attributes of Bioaccumulation in Streams. Pathways of OCs into stream food webs are poorly understood (*13*). Marine and lake systems are often autotrophic, so studies have focused mainly on the water−phytoplankton−zooplankton pathway of OCs into pelagic food webs and the role of benthic invertebrates in moving contaminants from sediment to consumers (*1, 29, 35*). Streams are more heterotrophic than lentic and marine systems, and most streams have two main sources of organic matter inputs, autochthonous benthic algae (i.e., biofilm) and allochthonous terrestrial leaf detritus (i.e., CPOM, ref *36*). Biofilm (a mix of autotrophs,

heterotrophs, and adhering detritus in a polysaccharide matrix (*36*)) provides a large surface area for uptake and adsorption from the water column and plays a key role in transferring PCBs to stream consumers (*5, 6, 37*). In contrast, the role of leaves in uptake and transfer of OCs in streams has received little attention. Temperate woodland streams receive major seasonal inputs of leaves, which are rapidly colonized by microbes (*36*). Conditioned leaves also provide a large surface area for adsorption of OCs in streams, which are then directly available to consumers such as shredding insects. PCB concentrations in leaves and biofilm are similar in streams (ref*13* and this study), suggesting that leaf detritus is also an important vector for OC transfer to higher trophic levels. Indeed, Berglund et al. (*13*) found that PCBs in brown trout (*Salmo trutta*) were positively correlated with degree of heterotrophy among streams. However, they attributed this finding to increased periphyton density (resulting from lower grazing pressure) in their more heterotrophic streams rather than direct transfer of PCBs from leaves to higher trophic levels. Additional studies are warranted to clarify the role of conditioned leaves in OC biomagnification in stream food webs.

Stream macroinvertebrate communities characteristically demonstrate high species and trophic diversity, and we sampled a large pool of macroinvertebrates (27 taxa) to fully characterize the trophic relationships, PCB concentrations, and congener patterns in this important group of stream consumers. PCBs in macroinvertebrates were less predictable than those in other matrices. Concentrations were often lower than predicted by TP, similar to results from fugacity-based models for macroinvertebrates in Lake Ontario (*31*). The largest negative residuals were primary consumers (Elmidae, *Pycnopsyche*, and Baetidae) in the shredder and grazer trophic guilds. TP may overestimate PCBs in macroinvertebrates because of their small body size and high growth rates. For example, small size classes of fishes with high growth rates have lower concentrations and shorter half-lives of PCBs compared with larger, slower growing individuals (*32, 38*). Likewise, bioconcentration is more important than dietary biomagnification for small species such as macroinvertebrates (*1, 16, 31*), suggesting that diet-based variables like TP will be less predictive of OCs in these organisms compared with larger consumers at higher trophic levels.

Contaminants in streams are a serious concern both in terms of ecosystem health and human exposure from streams providing water and sustenance. Streams are productive systems exporting energy, organic matter, and contaminants to downstream water bodies and riparian zones. Here, we show that δ^{15}N-derived TP strongly predicts contaminant concentration and composition in a complex stream food web. These relationships underscore the utility of TP as a robust tool for predicting contaminant exposure or risk to stream consumers and for identifying important processes driving biomagnification in streams.

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Supporting Information Available

Table S1: List of measured PCB congeners, analytical chemistry and trophic characterization; Figure S1: ordination analysis of congener composition. This information is available free of charge via the Internet at http://pubs.acs.org.

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