Spider-Mediated Flux of PCBs from Contaminated Sediments to Terrestrial Ecosystems and Potential Risks to Arachnivorous Birds†

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We investigated aquatic insect utilization and PCB exposure in riparian spiders at the Lake Hartwell Superfund site (Clemson, SC). We sampled sediments, adult chironomids, terrestrial insects, riparian spiders (Tetragnathidae, Araneidae, and *Mecynogea lemniscata*), and upland spiders (Araneidae) along a sediment contamination gradient. Stable isotopes (δ^{13}C, δ^{15}N) indicated that riparian spiders primarily consumed aquatic insects whereas upland spiders consumed terrestrial insects. PCBs in chironomids (mean 1240 ng/g among sites) were 2 orders of magnitude higher than terrestrial insects (15.2 ng/g), similar to differences between riparian (820−2012 ng/g) and upland spiders (30 ng/g). Riparian spider PCBs were positively correlated with sediment concentrations for all taxa ($r^2 =$ 0.44−0.87). We calculated spider-based wildlife values (WVs, the minimum spider PCB concentrations causing physiologically significant doses in consumers) to assess exposure risks for arachnivorous birds. Spider concentrations exceeded WVs for most birds at heavily contaminated sites and were ~14-fold higher for the most sensitive species (chickadee nestlings, *Poecile* spp.). Spiders are abundant and ubiquitous in riparian habitats, where they depend on aquatic insect prey. These traits, along with the high degree of spatial correlation between spider and sediment concentrations we observed, suggest that they are model indicator species for monitoring contaminated sediment sites and assessing risks associated with contaminant flux into terrestrial ecosystems.

Introduction

Sediments are primary sources of contaminants that bioaccumulate in aquatic food webs (*1*). Risk is widespread, with ~10% of U.S. surface waters underlain by sediments sufficiently contaminated to pose risks to humans or wildlife (*1*). Polychlorinated biphenyls (PCBs) are a primary contaminant of concern in freshwaters, and nearly 2 million lake hectares and 209,000 river kilometers in the U.S. have fish consumption advisories for PCBs (*2*). Quantifying the fate and transport of persistent contaminants like PCBs is a crucial step in mitigating contaminated sites and managing risks to humans and the environment (*3*). Contaminant transport is often attributed to physical processes (e.g., currents), but recent studies emphasize the role of biological transport as a key process regulating contaminant exposure in organisms or environments beyond contaminated areas (*4–7*).

Emergent aquatic insects are important vectors of contaminant transport from aquatic to terrestrial ecosystems. Insects emerging from contaminated systems have high concentrations of persistent contaminants (*8–10*), and chironomids (Diptera, Chironomidae) transfer substantial contaminant mass to terrestrial ecosystems because of their high productivity (*11*, *12*). Insect-borne contaminants bioaccumulate in terrestrial invertivores including birds (*13–15*) and spiders (*7*). Riparian spiders are important predators of aquatic insects (*16*, *17*), and those living next to contaminated sediment sites accumulate high levels of contaminants (*7*, *18*). These contaminants are transferred to higher trophic levels of the terrestrial food web (*18*), suggesting that spiders play a key role in mediating contaminant flux from aquatic to terrestrial ecosystems.

We investigated trophic transfer and bioaccumulation in riparian spiders adjacent to a reservoir highly contaminated with PCBs (*19*). Our first objective was to establish trophic linkages between spiders and aquatic insects through analysis of natural abundance of stable carbon (δ^{13}C) and nitrogen (δ^{15}N) isotopes. These isotopes are routinely used to quantify trophic interactions between aquatic and terrestrial food webs and to track organic matter and contaminant flow within and between ecosystems (*17*, *20–22*). We hypothesized that aquatic insects would demonstrate higher PCB concentrations than terrestrial insects, and that riparian spiders consuming aquatic insects would have higher PCB concentrations than upland spiders feeding on terrestrial insects. Our second objective was to determine if spider and sediment PCB concentrations were correlated along a contamination gradient. If so, spiders could be useful indicator species for monitoring contaminated sites (*23*, *24*). Our final objective was to assess risks of spider consumption to their predators, in this case arachnivorous birds. This study documents longitudinal patterns in PCB accumulation in various spider taxa dwelling at the water−land interface. We conducted a concurrent study investigating the lateral flux of aquatic insects and PCBs into riparian forests and their associated food webs (*25*).

Experimental Section

Study Area. Lake Hartwell (South Carolina) was contaminated by PCBs discharged from the Sangamo-Weston capacitor plant located on a tributary ~25 km upstream of the reservoir. The plant operated from 1955 to 1977, discharging ~181.4 MT of PCBs into the aquatic environment (*19*). High levels of PCBs in sediment and organisms within the Twelvemile Creek arm (TCA) of Lake Hartwell are well documented and ongoing (Supporting Information, Figure S1; *19*, *26*). Sediment concentrations peak near transects O and N (Figure S1), then decline down-lake to T6 (*26–28*). Deposited sediment concentrations were lower above transect O due to accretion of low organic-content sands (with lower PCB concentrations) exported from Twelvemile Creek (*19*, *26*). Concentrations decline rapidly down-lake of T6 due to inputs of uncontaminated sediment and water from the Keowee River arm (*28*).

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Sample Collection. We sampled sediment and biota from June to August 2007 at 11 sites in the TCA (Figure S1). Sediment transects were oriented perpendicular to shore, and samples were collected at the center of the inundated stream channel and at 25 and 75% of lake width ($n = 3$ for each transect). Surface sediments (0−10 cm depth) were collected by push coring at least 30 cm using a 70-cm diameter polycarbonate core.

Spiders were collected from four sampling quadrats spanning 50 m of shoreline on both banks up- and down-lake of the sediment transect. Spiders were collected at night from vegetation overhanging the water or within 2 m of the shoreline. Samples were composites of several individuals. We collected three taxa, Tetragnathidae (*Tetragnatha* spp.), Araneidae (primarily *Araneus, Eustala, Gasteracantha,* and *Neoscona* spp.) and *Mecynogea lemniscata* (basilica spider), which vary in habitat use and feeding behavior. Tetragnathids are obligate riparian species, build weak, horizontal orb webs, and specialize in consumption of aquatic insects (*16, 29, 30*). Araneid spiders are distributed from riparian to upland habitats, build strong, vertical orb webs, and feed on aquatic and terrestrial insects (*16, 31*). Basilica spiders are also in the family Araneidae, but build permanent, colonial, dome webs in shrubs and prey heavily on terrestrial insects (*32*). Where possible, one replicate of each taxon from each quadrat was analyzed for PCBs. Individuals were randomly selected from all quadrats and pooled into three composite samples for stable isotope analysis. Upland populations of araneids (dominated by the same genera as riparian araneids) were also sampled at transects O, I, and T-6, which corresponded with high, medium, and low sediment PCB concentrations (Figure S1). Upland spiders ($n = 3$ per site) were collected along a 100-m transect parallel to the lake shoreline and located 30 m inland.

Collection of emergent aquatic insects focused primarily on adult chironomids. These were abundant and ubiquitous across the study area, facilitating sample collection and among-site comparisons. Other adult aquatic insects were present, but their abundance was low and their occurrence was sporadic among locations. Chironomids were collected from boats trolled across the width of each transect at night. Insects were attracted to boats using fluorescent and incandescent light and collected using sweep nets. Three composite samples were collected where possible based on available biomass. Samples were sorted in the laboratory to remove nontarget insects and split for PCB and stable isotope analysis. Terrestrial insects were sampled using canopy traps (Supporting Information) deployed in the forest at transects O, I, and T-6 (*25*). Traps were deployed at 0, 5, 10, 20, and 30 m from the forest-lake edge. Insects were identified to family and categorized as herbivores, omnivores, or predators. Stable isotopes were analyzed for individual organisms or composite samples depending on body size ($n = 82$). Composite samples for PCB analysis were pooled differently for each site. At site O, insects were composited by trophic guild ($n = 3$). At site I, composite samples were drawn from insects consolidated from all traps ($n = 3$). At site T-6, samples from each canopy trap were composited into a single sample ($n = 5$). Aquatic insect larvae were collected for stable isotope analysis in summer 2005 and 2006 using Hester-Dendy samplers deployed at sites M, N, and O (Figure S1). Taxa collected included chironomids ($n = 15$), Ephemeroptera ($n = 4$), Plecoptera ($n = 1$), and Trichoptera ($n = 7$). These data were included to provide a broader comparison of isotopic differences between aquatic and terrestrial insects. All sediment and arthropod samples were placed on ice, frozen in portable freezers for transport, and then stored at −20 °C until analyzed.

Chemical Analyses. Detailed methods for sample extraction, PCB quantification, and quality control procedures for PCB and stable isotope analyses are provided in Supporting Information. Analysis for PCB congeners was by gas chromatography-electron capture detection (GC-ECD, Agilent 6890) adapted from EPA method 8082. This method quantifies 126 GC peaks representing 141 congeners (Table S1), which were summed to calculate total PCBs (ΣPCBs). Minimum detection limits ranged from 0.17 to 8.83 ng g^{-1} among congeners. Analytes not detected were assigned a 0 value. A 5-mL aliquot of extract was analyzed for lipids using the gravimetric method.

Samples for $\delta^{13}C$ and $\delta^{15}N$ analysis were freeze-dried, milled, and homogenized. Homogenates were combusted to CO_2 and N_2 and analyzed in a Carlo Erba NA 1500 CHN analyzer connected to a Finnigan Delta isotope ratio mass spectrometer. Reference standards were PeeDee Belemnite Carbonate for $\delta^{13}C$ and atmospheric N_2 for $\delta^{15}N$. Lipid content can influence $\delta^{13}C$ values (*33*), but lipids were not extracted prior to analysis. Lipid concentrations were uniformly low among samples (≤5%, Table S1), and, at these levels, extraction or mathematical normalization has little influence on $\delta^{13}C$ values (*33*).

Derivation of Spider-Based Avian Wildlife Values. We calculated wildlife values (WVs) for arachnivorous birds at Lake Hartwell following the methods of Lazorchak et al. (*34*) and U.S. EPA (*35*). Detailed calculation methods are provided in Supporting Information and Table S2. Wildlife values reflect the minimum PCB concentrations in spiders, consumed by birds in normal proportions of total diet, required to create physiologically significant doses (*35*). Lower WVs are associated with higher risk. We developed WVs for 11 species and life stages of birds that had published life-history data needed for calculations (Table 1, Table S2). All species are year-round residents except Marsh Wrens (seasonal migrants) and House Wrens (summer breeders). Most birds considered also consume adult aquatic insects, which are contaminated with PCBs at Lake Hartwell, so spider-based WVs may not fully account for exposure risks. Likewise, WVs do not account for bird movements, and time spent foraging outside of contaminated areas would reduce risks.

We compared avian WVs with spider PCB concentrations to assess the relative risk to birds consuming riparian spiders. We calculated relative risk as spider concentration/WV to determine the proportional difference between dietary concentrations and those expected to cause adverse effects in birds. Spider concentrations exceed avian WV when relative risk values are >1. Relative risk was calculated for each sampling quadrat and was determined separately for araneid spiders (the most contaminated taxon) and for all spider taxa combined (mean concentration among taxa). The latter approach is conservative and assumes equal consumption across taxa, rather than specialized consumption of araneids.

Data Analyses and Mapping. Isotopic differences between adult chironomids and terrestrial insects were tested using a two-tailed *t* test with unequal variances, and differences among riparian and upland spiders were tested using analysis of variance (ANOVA) with a posthoc Tukey's HSD test. Samples were pooled among sites and were treated as individual replicates for among-group comparisons. Values within each group (adult chironomids, terrestrial insects, and spider taxa) were normally distributed (Shapiro−Wilk test). We used a standard single isotope ($\delta^{13}C$), two-source (adult chironomids versus terrestrial insects) mixing model (i.e., ISOERROR) to calculate source proportions of spider prey (*36*). We assumed one trophic level between insects and spiders, and corrected spider $\delta^{13}C$ for trophic fractionation using a value of 0.4‰ (*37, 38*). We did not use a two isotope mixing model due to uncertainty in correcting trophic fractionation in $\delta^{15}N$ for spiders. A mean fractionation factor (i.e., $\Delta\delta^{15}N$) of ~3‰ is commonly used (*37, 39*), but $\Delta\delta^{15}N$ for spiders is likely much lower. Invertivores (e.g., spiders)

TABLE 1. Wildlife Values (WVs) for Protection of Avian Spider Predators (Low Values Indicate Greater Risk)[a]

common name and life stage	species	wildlife values (ng/g spider)	relative risk, Araneid (range)	relative risk, all spiders (range)
adult				
American kestrel	*Falco sparverius*	13230	0.01−0.55	0.02−0.33
American robin	*Turdus migratorius*	5752	0.03−1.28	0.04−0.77
eastern bluebird	*Sialia sialis*	4295	0.05−1.71	0.05−1.03
Carolina wren	*Thryothorus ludovicianus*	2667	0.07−2.75	0.09−1.65
house wren	*Troglodytes aedon*	3318	0.06−2.21	0.07−1.33
marsh wren[b]	*Cistothorus palustrus*	4900	0.04−1.50	0.05−0.90
marsh wren[c]	*C. palustrus*	11855	0.02−0.62	0.02−0.37
nestling				
American kestrel (1−3 d)	*F. sparverius*	26459	0.01−0.28	0.01−0.17
American kestrel (7−10 d)	*F. sparverius*	8652	0.02−0.85	0.03−0.51
chickadee (1 d)	*Poecile atricapillus/P. gambeli*	794	0.25−9.25	0.29−5.55
chickadee (12 d)	*P. atricapillus/P. gambeli*	529	0.37−13.88	0.43−8.34

[a] Relative risk (wildlife value/spider PCB concentration) was calculated assuming that spiders consumed as a normal proportion of diet consisted of 100% araneid spiders (relative risk, araneid) or consisted of all spider taxa (relative risk, all spiders). Minimum and maximum values are for locations with the lowest and highest spider concentrations, respectively. [b] Summer diet. [c] Winter diet.

have $\Delta\delta^{15}N$ of 1.4‰ (*39*), and field studies have reported negligible or small differences in $\delta^{15}N$ between aquatic insects and their spider predators (*7, 31, 38*, this study). Samples from all sites were combined within groups for mixing model analysis. We used linear regression to determine relationships between mean sediment and biota ΣPCB concentrations (as ng g^{-1} wet weight and lipid) calculated for each site. Sediment samples at sites H and T6 (Figure S1) had poor surrogate recoveries and were excluded from statistical analyses. We estimated sediment ΣPCB values at sites H and T6 relative to concentrations that we measured at sites L and O (Figure S1), respectively, based on surface concentrations measured between 1987 and 2001 (*26, 28, 40*). Estimated values based on historical trends are presented for graphical purposes, but were excluded from statistical analyses.

We developed maps of sediment and tetragnathid ΣPCB concentrations and relative risk for chickadee nestlings to illustrate spatial variation and concordance among these measures within the TCA. Sediment concentrations were generated using data from each of the three sample points along each transect. Sediment values for sites H and T6 were estimated concentrations based on historical trends (described above). Tetragnathid ΣPCBs and spider-based relative risk values were generated using data from each spider sampling quadrat. Sediment and shoreline values between sampling points were interpolated using the spline with barriers interpolation tool in ArcGIS 9.3 (ESRI, Redland, CA).

Results

We used $\delta^{13}C$ and $\delta^{15}N$ values to determine if aquatic and terrestrial prey had different isotopic signatures and if these differences could be used to infer prey use among spiders. Aquatic and terrestrial insects had distinct isotopic signatures. Adult chironomids were more depleted in $\delta^{13}C$ and enriched in $\delta^{15}N$ than terrestrial insects (Figure 1; $\delta^{13}C$, $t = -11.6$, $p < 0.0001$; $\delta^{15}N$, $t = 18.9$, $p < 0.0001$), with similar differences observed between aquatic insect larvae and terrestrial insects. Isotopic signatures of riparian and upland spiders reflected differences in prey sources, indicating that riparian spiders consumed a high proportion of aquatic insects whereas upland araneids consumed terrestrial insects (Figure 1). Riparian araneids and tetragnathids were significantly depleted in $\delta^{13}C$ compared with basilica and upland araneids (ANOVA, $F = 6.8_{3,96}$; $p < 0.0003$; Tukey $p < 0.05$). All riparian taxa were significantly enriched in $\delta^{15}N$ compared with upland araneids, and tetragnathids had higher $\delta^{15}N$ compared with other riparian taxa ($F = 37.5_{3,96}$; $p < 0.0001$; Tukey $p <$ 0.05). Mixing model estimates of aquatic insect consumption by spiders were 91% (±9.8 SE) for tetragnathids, 86% (±12.6) for araneids, 51% (±7.0) for basilica spiders, and 30% (±6.0) for upland araneids.

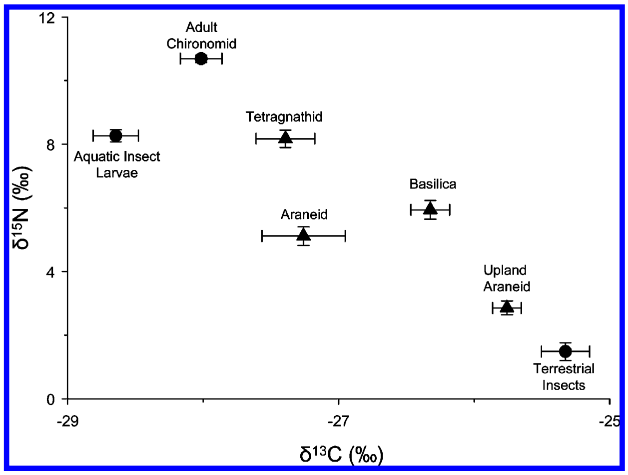

FIGURE 1. $\delta^{13}C$ and $\delta^{15}N$ values (mean ± SE) for insects (circles) and spiders (triangles) at Lake Hartwell, South Carolina. Data were pooled among all sites.

Sediment ΣPCB concentrations varied from 220 to 1340 ng g^{-1} wet weight among sites, similar to the range of adult chironomid values (410−1850 ng g^{-1}, Table S3). Concentrations of ΣPCBs in nonpredatory (3−4 ng g^{-1}), predatory (145 ng g^{-1}), and all terrestrial insects combined (15 ng g^{-1}) were 1−3 orders of magnitude lower than the highest chironomid concentration. Total PCBs were high in riparian spiders, with maximum site concentrations of 4262, 2073, and 1602 ng g^{-1} for araneids, tetragnathids, and basilica spiders, respectively (Table S3). Concentrations in upland spiders (30 ng g^{-1}) were 1−2 orders of magnitude lower than those in riparian spiders from the most contaminated sites, consistent with large differences between adult chironomids and terrestrial insects.

As expected, sediment ΣPCB concentrations peaked near the top of the TCA (just below the sand depositional zone) and declined with distance down-lake (Figure 2). Adult chironomid concentrations were highly variable among sites and demonstrated no longitudinal pattern. Concentrations in all spider taxa corresponded with measured sediment concentrations, peaking near the top of the TCA and then declining down-lake. PCB concentrations among sites were consistently highest in araneids, intermediate in tetra-

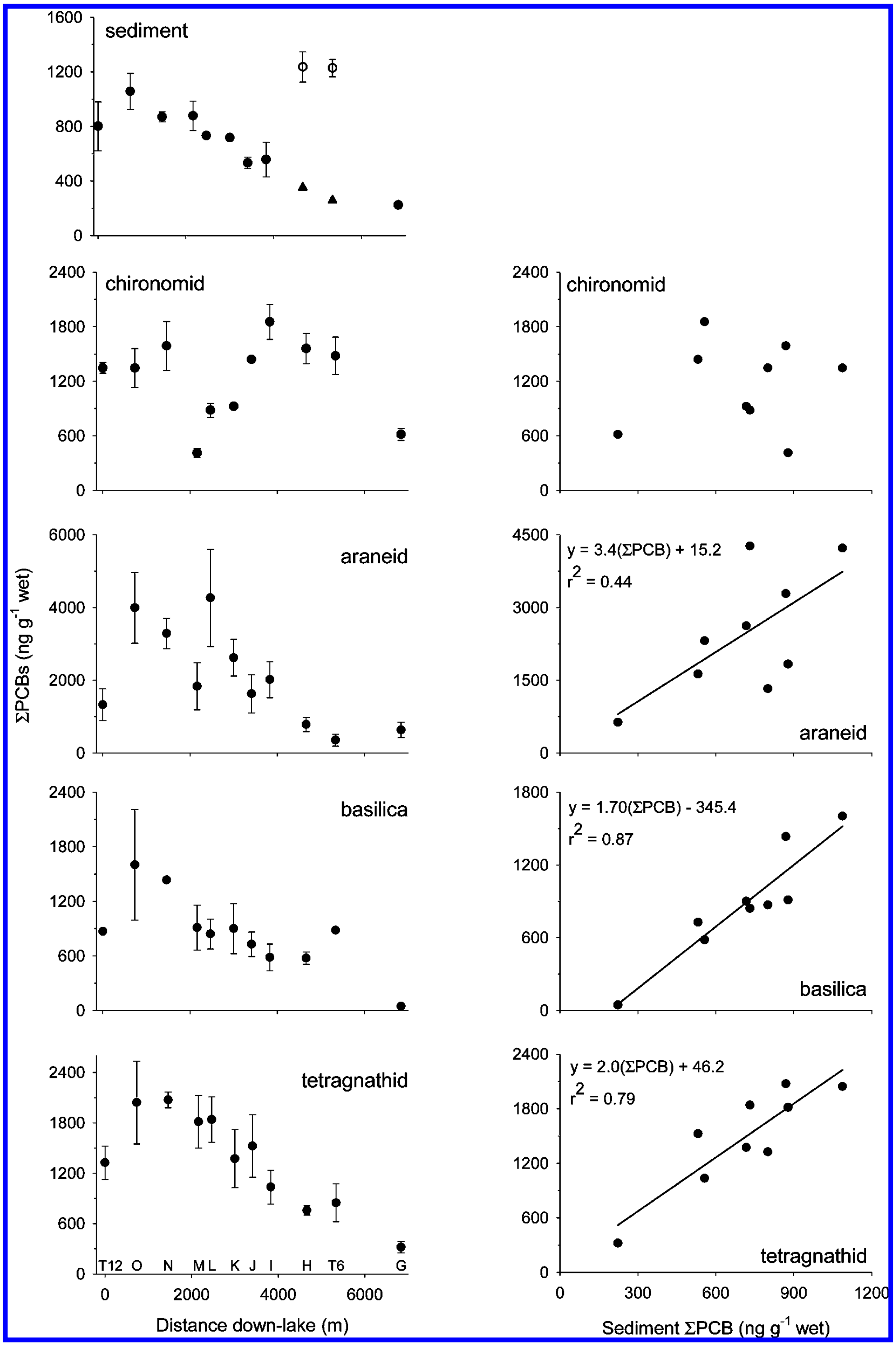

FIGURE 2. Left panel: Longitudinal trends in sediment and biota ΣPCB concentrations (mean wet weight ± SE). Site locations for longitudinal plots are provided in the bottom graph and referenced in Figure S1. Open symbols in sediment plot denote samples with poor recovery of surrogate and internal standards. Triangles in sediment plot represent estimated surface concentrations at site H and T6 relative to sites L and O, respectively, based on prior sediment surveys (see methods). Right panel: Relationships between sediment and biota ΣPCB concentrations (wet weight). Only significant trend lines are shown (araneid $p < 0.05$; basilica $p < 0.0002$; tetragnathid $p < 0.001$). Points represent site means excluding sites H and T6 ($n = 9$). The scale of the y-axis varies among matrices in both panels.

gnathids, and lowest in basilica spiders (Figure 2). This pattern held when concentrations were corrected for lipid content (results not shown).

Sediment ΣPCB concentrations were unrelated to chironomid concentrations ($p > 0.72$), but were positively correlated with concentrations in all riparian spider taxa (Figure 2). Sediment concentrations explained 44−87% of the variation among taxa, with the strongest relationship between sediment and basilica spiders. Including lipid-normalized data in models improved the relationships for araneids ($r^2 = 0.52$) and tetragnathids ($r^2 = 0.89$), but weakened the relationship with basilica spiders ($r^2 = 0.69$). ΣPCB concentrations in araneids were ~3.5-fold, tetragnathids ~2-fold, and basilica spiders ~1.7-fold higher on

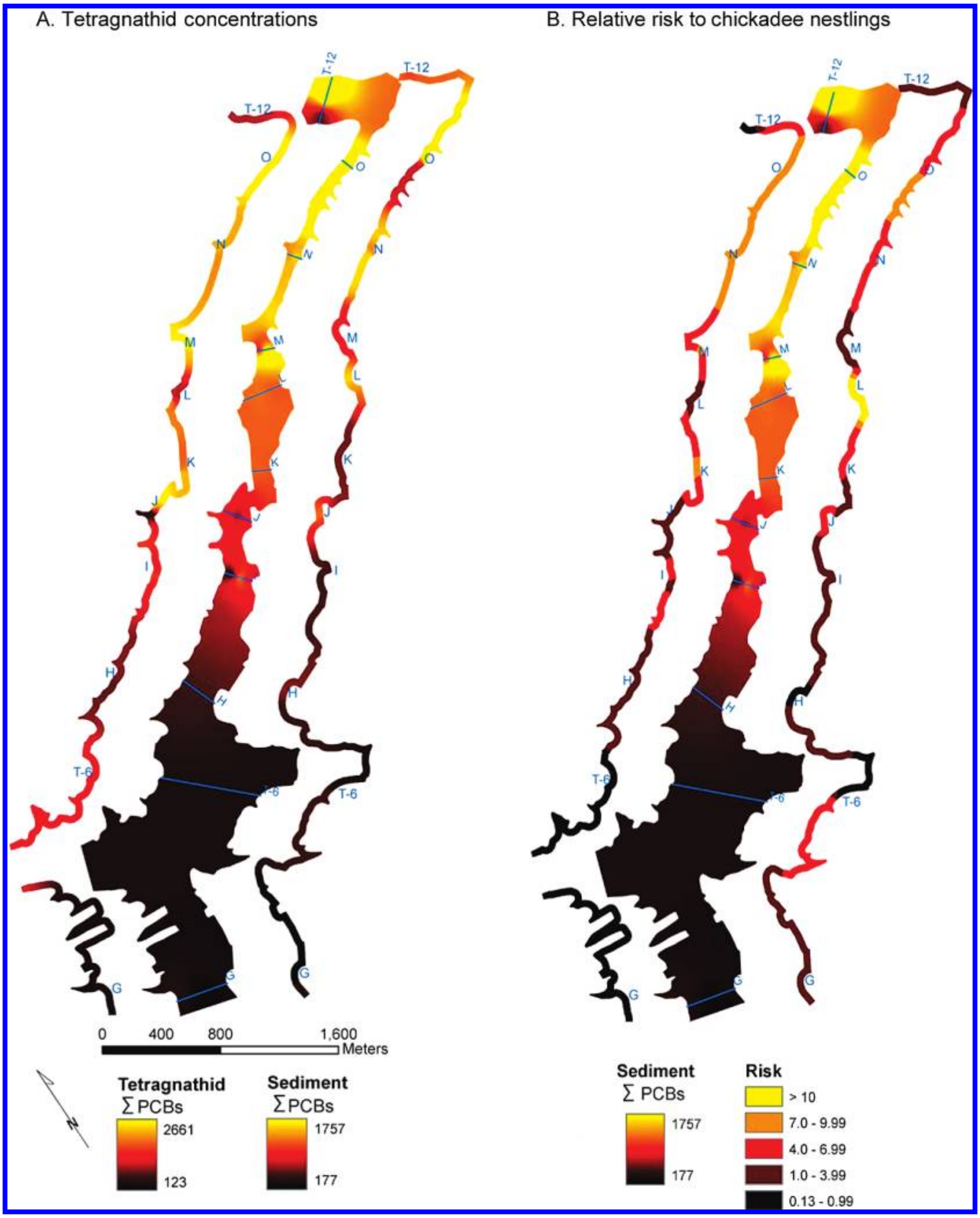

FIGURE 3. (A) Interpolated tetragnathid and sediment PCB concentrations in the Twelvemile Creek Arm of Lake Hartwell. Tetragnathid concentrations are depicted in ribbons flanking the lake. (B) Distribution of relative risk to chickadee nestlings consuming riparian araneid spiders along Lake Hartwell. Relative risk (araneid ΣPCB concentration/chickadee nestling WV) is depicted in ribbons flanking the lake. Sample locations are shown on lake and shoreline ribbons. Note separate scales for tetragnathid and sediment concentrations and relative risk values.

average than sediment concentrations, as indicated by regression slopes (Figure 2). Sediment and tetragnathid PCB concentrations were strongly correlated ($r^2 = 0.79$), and these concentrations show strong concordance when mapped on Lake Hartwell and its shoreline (Figure 3A). Small-scale spatial variation is evident on the map (e.g., opposite banks at a given transect may be colored differently), because the interpolated values were derived from individual point measurements along the sediment transects and shoreline quadrats. This spatial variability is obscured in the regression models, which were derived using site mean values.

Avian wildlife values (WVs) for PCBs varied from 529 to 26,459 ng g^{-1} among species, life stage, and season (Table 1). Lower WVs were associated with smaller body size, higher ingestion rates, and a greater proportion of spiders in the diet (Supporting Information, Table S2). Small-bodied adult and nestling passerine birds (e.g., carolina wren and chickadee) had the lowest WV values and the greatest exposure risk from spider consumption. Minimum relative risk values for araneid consumption varied from 0.01 (American kestrel nestling) to 0.37 (chickadee nestling), and maximum values ranged from 0.28 to 13.88 for these species. Araneid consumption at the most contaminated location would result in PCB exposures ranging from ~30% to 1400% of the WV among birds. Maximum relative risk values were >1 in 7 of 11 cases, indicating that the majority of birds considered would be exposed to potentially harmful PCB levels when foraging at the most contaminated locations. Relative risk was lower when calculated for all spiders (Table 1), because tetragnathid and basilica spiders had lower PCB concentrations than araneids. However, maximum relative risks calculated using all spiders were >1 in five cases, and PCB levels in the most contaminated spiders were 8.3-fold higher than the WV for chickadee nestlings. Risk for chickadee nestlings was highest in the upper reaches of the TCA, corresponding with highest sediment and spider concentrations (Figure 3B). Relative risk was >1 at most sites, indicating the potential for harmful exposures throughout most of the study area.

Discussion

Vast portions of the world's aquatic resources are polluted with persistent contaminants at levels that are toxic to wildlife (*1, 2, 41*). These contaminants are transported to terrestrial systems through movement (e.g., aquatic insects) or by direct predation on aquatic species by terrestrial predators (*42*). Indeed, piscivorous seabirds bioaccumulate contaminants from marine fishes and then transport them to remote, relatively pristine freshwater systems (*4*), highlighting the porous nature of ecosystem boundaries and the important role of biological vectors in linking seemingly disconnected ecosystems (*5, 43*). Given their ubiquity, productivity, and propensity to accumulate persistent contaminants, aquatic insects are important biotransporters of contaminants (*9, 11, 12*). Aquatic insects provide critical energy subsidies to terrestrial ecosystems, fueling riparian food webs and exposing terrestrial consumers to aquatic contaminants (*7, 13, 16, 17*, this study).

Our results clearly indicated this trophic mechanism of aquatic−terrestrial contaminant flux. Riparian spiders consumed contaminated aquatic insects (as inferred from stable isotope values), resulting in much higher levels of PCBs than upland spiders consuming relatively uncontaminated terrestrial insects. Additional diet data (e.g., web prey surveys) would be needed to fully confirm this finding. Our results were relatively straightforward to interpret because terrestrial and aquatic prey and their consumers were isotopically distinct and had vastly different contaminant concentrations. However, this will not likely be the case in all systems, particularly in regard to stable isotopes (*22*), so this approach should be applied on a case-by-case basis.

We used adult chironomids as a model insect species to investigate aquatic to terrestrial contaminant flux because they typically dominate freshwater insect assemblages and are capable of transporting substantial quantities of aquatic contaminants (*11, 12, 15*). Chironomids effectively demonstrated trophic transfer in this system (i.e., isotopic correspondence with riparian spiders and much higher PCB concentrations than terrestrial insects), yet their concentrations were unrelated to sediment concentrations. The lack of correspondence may be related to the short life span and exposure time of chironomids. Adult chironomids were sampled in summer when their larval stage lasts only a few weeks in the warm climate of South Carolina. Small, rapidly growing organisms respond quickly to changes in local conditions and typically demonstrate high spatial and temporal variability in chemical signals (*24, 44*). Movement patterns of adult chironomids are also unknown. Movement could have been affected by wind carrying chironomids between sites or by our use of light to attract adults at sampling locales. Concentrations of PCBs are also 8.5-fold higher in male than female chironomids (*15*). We did not sex chironomids prior to PCB analysis, so inconsistent sex ratios among samples could have contributed unexplained variability in our study.

Spider PCB concentrations, however, tracked spatial variation in sediment PCB concentrations. Relationships for spiders may have been stronger than that for adult chironomids because of their longer life span (i.e., one year) or their sedentary nature. The strength of these relationships suggests that spiders consume insects emerging at a local scale relevant to our 100 m sampling frame (i.e., spiders sampled 50 m up- and down-lake of the sediment transect). Concentrations among taxa varied considerably. Basilica spiders had the lowest concentrations, consistent with greater reliance on terrestrial insect prey (*32*, this study). However, araneid concentrations were twice as high as tetragnathids, even though isotopic analysis indicated that they consumed similar levels of aquatic insects. We observed araneids consuming tetragnathid spiders during sample collection, and occasional intraguild predation by araneids may increase their exposure to persistent contaminants. Differences in isotopic fractionation rates among taxa could contribute error to the estimates of aquatic prey consumed. Upland araneids consumed an estimated 30% aquatic prey, and this is inconsistent with their low PCB concentrations (30 ng g^{-1}) that would suggest much lower consumption of aquatic insects. More empirical and mechanistic studies are needed to identify physiological and toxicokinetic processes contributing to these interfamily differences.

Birds bioaccumulate persistent contaminants by eating aquatic insects (*13–15*), yet birds consuming invertebrate predators such as spiders may be at greater risk of exposure because they feed higher in the food chain, thereby increasing the opportunities for biomagnification (*18*). Spider PCB concentrations in Lake Hartwell pose substantial risk to birds, exceeding derived WVs for many species at the most contaminated sites. Risk was most acute for chickadee nestlings due to low mass and high ingestion rates. The low WV for chickadee nestlings is likely representative of small passerines such as house wrens that also grow from 1 g as hatchlings to ~10 g as adults (*45*). While harmful exposures are likely to occur over time, high concentrations in spiders could result in acute exposures from an episodic feeding event. Measured araneid concentrations at the most contaminated site were >6000 ng g^{-1}. At these levels, small-bodied passerine nestlings could be exposed to physiologically significant doses of PCBs by ingesting a single, typically sized araneid spider (e.g., 130 mg).

Utilizing Spiders in Risk Management of Contaminated Sediment Sites. Terrestrial exposure from aquatic sources is a primary risk at contaminated sediment sites, and identification of indicator species is a critical need for site risk assessment (*3*). Effective indicators should integrate the contaminant signal spatially and temporally, be easy to sample, process, and quantify analytically, be easy to interpret, and be comparable across ecosystems (*23, 24*). Prior studies recommended adult aquatic insects as indicators of contaminated sediment contamination and associated risk in terrestrial systems (*9*). We used adult chironomids as a model insect because their ubiquity and abundance facilitates sample collection as well as cross-system comparisons. However, adult chironomids were ineffective indicators because they failed to spatially integrate the sediment contaminant signal (*23*). It is feasible that larval chironomids (or other aquatic insects) may be better indicators of local sediment conditions because they are likely to be more sedentary than winged adults.

Riparian spiders met several criteria for effective indicator species. They integrated the contaminant signal spatially, as indicated by significant correlations between sediment and spider concentrations. They were easily sampled after dusk when they were actively building webs. They were abundant, which is typical of riparian spider populations (*16, 17*), facilitating the collection of biomass required for chemical analyses. Interpretation of spider concentrations is straightforward as they are sedentary (e.g., basilica spiders build permanent webs) and rely heavily on aquatic insect prey in riparian habitats (*16, 17*). Tetragnathid spiders are particularly suited as indicator species because they are specialized predators of aquatic insects (*16, 29, 30*) and are obligate riparian species globally distributed around freshwater systems (*30*). These generalized traits of riparian spiders (e.g., habitat and prey specificity, ubiquity, and abundance) lend themselves well to cross-system comparison.

Spiders have served as model terrestrial predators in ecological studies (*46*), yet they are underutilized for assessing exposure pathways of persistent contaminants in aquatic and terrestrial food webs. The large size of many contaminated sediment sites complicates their assessment and implementation of remedial actions, underscoring the need for reliable indicators of ecosystem condition (*3*). Spiders may play a key role in regulating aquatic to terrestrial flux of contaminants from freshwater systems (*7, 18*), and the strong correlations we found between some spiders and sediment PCB concentrations indicates that they are useful indicators for monitoring the efficacy of site management actions. Spider exposure results from complex processes including contaminant uptake by benthic insects, maturation, emergence, and flight of insects, and predator−prey interactions operating across space and time. As such, changes in spider contaminant concentrations could provide an integrative measure of ecosystem recovery from contaminated sediment. Additionally, their relatively short life span make them ideally suited to reflect changes in ecosystem and sediment concentrations over the time frame of typical remedial actions (1−3 years) as opposed to longer-lived species (e.g., sport fish) that may reflect historic body burdens.

We used PCB data and spider-based WVs to develop integrated geospatial maps of contaminant sources, environmental concentrations, and their associated risks to ecological receptors of concern (*47*). The map of tetragnathid concentrations illustrated bioavailability, broadly defined as the ability of contaminants to interact with the biological world (*48*), and could serve as the baseline for monitoring changes in response to site remediation. By evaluating spider PCB concentrations within a risk framework (*3*), we generated spatially explicit risk assessments identifying species (or life stages) of birds at greatest risk of exposure and where harmful exposures are likely to occur. This analysis is a critical first step for identifying at-risk populations of sensitive species, for guiding future characterization of these populations, and for designing food web studies to quantify the flux of contaminants from spiders to avian predators. Likewise, the geospatial mapping approach is a powerful tool for simplifying the complexity of large contaminated sites for managers and experts and for communicating with stakeholder groups that may have less technical expertise (*47*).

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Supporting Information Available

Canopy trap methods, PCB extraction, quantification, and quality assurance (QA); stable isotope QA; wildlife value calculations and bird traits; PCB, lipid, and stable isotope data. This information is available free of charge via the Internet at http://pubs.acs.org/.

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