The distance that contaminated aquatic subsidies extend into lake riparian zones

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Abstract. Consumption of emergent aquatic insects by terrestrial invertebrates is a poorly resolved, but potentially important, mechanism of contaminant flux across ecosystem borders leading to contaminant exposure in terrestrial invertivores. We characterized the spatial extent and magnitude of contaminant transfer from aquatic sediments to terrestrial invertebrate predators by examining riparian araneid spiders, terrestrial insects, and emergent aquatic insects for stable isotopes and polychlorinated biphenyls (PCBs, sum of 141 congeners) at Lake Hartwell, (Clemson, South Carolina, USA). PCB concentrations in aquatic insects were orders of magnitude higher than in terrestrial insects. Aquatic insect consumption by spiders (as indicated by $\delta^{13}C$ and $\delta^{15}N$), PCB concentrations in spiders, and aquatic prey availability were greatest at the shoreline and declined inland, while terrestrial prey availability was invariant with distance. These patterns indicate PCB transfer to spiders through consumption of emergent aquatic insects extending to a distance of ~5 m inland. Measurable, but much lower, PCBs were present in insect predators dominated by social wasps up to 30 m inland. These results illustrate the importance of emergent insects as vectors of contaminant transfer from lake sediments to riparian food webs, and that spiders are key predators in this process.

Key words: aquatic insects; contamination; ecological subsidy; exposure; food web; lake; polychlorinated biphenyls (PCBs); riparian zone; spiders; tracers.

INTRODUCTION

Understanding processes within ecosystems requires accounting for the flow of materials between ecosystems (Polis et al. 2004). Landscape-level movement of materials has long been incorporated into the study of food webs with the concept of ecological subsidy, or donor-control of material originating from areas distant from locations of exploitation (Polis et al. 1997). Yet because ecological subsidy results largely from the consumption of materials that have simply moved from one ecosystem to another, contaminants can be transferred along with beneficial resources (Rasmussen and Vander Zanden 2004). Contaminant flux is a particularly important aspect of subsidies operating at the land-water ecotone because terrestrial consumers congregate in riparian habitats to exploit aquatic resources (Vander Zanden and Sanzone 2004) and because contamination of aquatic systems is remarkably widespread. For example, ~6 million lake hectares and ~1.5 million river kilometers are under fish consumption advisories in the United States, primarily due to high levels of persistent contaminants such as mercury and polychlorinated biphenyls (PCBs; U.S. Environmental Protection Agency 2007).

Adult aquatic insects provide an important energy subsidy to riparian consumers (Baxter et al. 2005, Ballinger and Lake 2006), and likely play a key role in regulating the flow of contaminants between aquatic and riparian food webs. Benthic aquatic insects such as burrowing mayflies (Ephemeroptera: *Hexagenia*) and midges (Diptera: Chironomidae) bioaccumulate persistent contaminants from surrounding sediments as larvae (Larsson 1984, Gobas et al. 1989) and retain contaminants upon emerging as adults (Larsson 1984, Fairchild et al. 1992). Indeed, emergent aquatic insects transport substantial quantities of contaminants from aquatic sediments to terrestrial ecosystems due to bioaccumulation in larval tissue and high secondary production (Menzie 1980, Fairchild et al. 1992). Walters et al. (2008), for example, estimated that aquatic insects export 6.1 g PCB/yr from a 25-km reach of Twelvemile Creek, the stream that drains into the site of this study. Midges in particular have been estimated to export 4.1 g Hg(II)/yr from a 2.1-km reach of a polluted stream (Runck 2007), and 20 μg PCB/m² from a site of high midge production (≥ 72 g·m²·yr⁻¹) and moderate midge contamination (251 ng/g) near a sewage plant (Larsson 1984). Exposure to sediment-derived contaminants then occurs in insectivorous terrestrial

predators such as spiders and herptiles (Walters et al. 2008), bats (Reinhold et al. 1999), and birds (Echols et al. 2004, Cristol et al. 2008).

However, mechanisms of trophic contaminant transfer between aquatic insects and terrestrial invertebrate predators and the spatial extent and magnitude of contaminant flux caused by aquatic insects in riparian habitats are poorly resolved. Evidence of terrestrial invertivore exposure through aquatic diets has been derived solely from stable isotope analysis, where riparian predators, including spiders, showed proportionately increasing PCBs with increasing aquatic prey reliance (Walters et al. 2008). Cristol et al. (2008) documented high mercury concentrations in araneid spiders along a contaminated river without identifying mechanisms of spider contamination and hypothesized that contaminant flux to terrestrial food webs could have occurred through insect emergence and/or overbank deposition. Indeed, many species of terrestrial spiders congregate along shorelines to feed on aquatic prey (Polis and Hurd 1995, Henschel et al. 1996, Baxter et al. 2005).

The distance that subsidies provided by emergent aquatic insects, and hence potentially associated aquatically derived contaminants, extend away from shorelines has been examined primarily in streams, where the distance of inland subsidy is highly variable and can be limited to a narrow band of riparian habitat (Sanzone et al. 2003, Briers et al. 2005, Gratton and Vander Zanden 2009). Examination of aquatic subsidy extension into lake and river riparian zones, where wind advection and greater secondary production could increase extension (Power and Rainey 2000), has been limited to ecosystems with non-forested riparian zones; specifically, the urbanized Laurentian Great Lake (North America), Lake St. Clair and its outlet the Detroit River (Kovats et al. 1996), and Icelandic lakes with heathland riparian communities (Gratton et al. 2008). No studies have examined impounded reservoirs, which behave ecologically as lentic ecosystems but can have morphologies similar to lotic ecosystems, and no studies have documented the spatial extent of contaminant transfer by aquatic insects into riparian habitats.

We analyzed spatial and trophic patterns of carbon and nitrogen stable isotopes ($\delta^{13}C$, $\delta^{15}N$) and PCB body burden in terrestrial and aquatic insects and araneid spiders at a reservoir with PCB-contaminated sediments. Our objectives were to characterize the trophic transfer of sediment-derived contaminants from aquatic insects to terrestrial invertebrate predators by quantifying the spatial extent and magnitude of contaminant flux. If aquatic insects are an important mechanism delivering aquatic contaminants to riparian food webs, then we expect that aquatic insects will have much higher concentrations of PCBs than terrestrial insects, especially non-predators. Likewise, spiders consuming aquatic insects should be much more contaminated than those consuming terrestrial prey.

We expect that aquatic insect availability, spider consumption of aquatic prey, and spider PCB concentrations will be greatest at the shoreline and decline rapidly with distance inland. If overbank deposition contributes to PCB exposure in spiders through consumption of contaminated terrestrial insects, then terrestrial insects should have elevated concentrations of PCBs, and those concentrations should be highest at sites subject to overbank contaminant deposition by floods.

METHODS

In 2007, we examined the Twelvemile Creek arm of Lake Hartwell, (Clemson, South Carolina, USA; area = 1.98 km^2, shoreline = 25.3 km), a regulated freshwater reservoir, which received ~181 metric tons (MT) of PCBs from an upstream industrial discharge between 1955 and 1978 (U.S. Environmental Protection Agency 1994). We established three sites in riparian zones adjacent to an in-lake sediment contamination gradient: an upstream "high-PCB site" (adjacent to 3.8 ± 2.4 μg/g PCB [mean $\pm$ SD] in sediments, shoreline elevation: 203.6 m), a mid-stream "mid-PCB site" (adjacent to 1.5 μg/g PCB in sediments, shoreline elevation: 201.8 m), and a downstream "low-PCB site" (adjacent to 0.93 μg/g in sediments, shoreline elevation: 204.2 m; Brenner et al. 2004; Appendix A: Fig. A1).

Chironomidae were chosen as representatives of emergent aquatic insects due to high abundance and ubiquitous presence across sample sites. Chironomidae were collected with sweep nets around an attractant light while slowly trolling the lake width adjacent to each riparian site at sunset to three hours after sunset. Emergent Hexagenia were sampled opportunistically in the riparian zone. Stable isotopes of aquatic insect larvae collected in summer 2005 and 2006 using Hester-Dendy samplers, including chironomids ($n = 15$), Ephemeroptera ($n = 4$), Plecoptera ($n = 1$), and Trichoptera ($n = 7$), were used to further compare the isotopic signatures of aquatic and terrestrial insect prey (Walters et al. 2010).

Terrestrial arthropods were sampled at 100 m long transects parallel to the shoreline. Five transects were established at each site 0, 5, 10, 20, and 30 m from the shore. All transects were in secondary growth, mature oak–hickory forests. Insects were continuously sampled from 11 June to 3 August 2007, using canopy traps with a 1.5-m^2 trap area (Sante Traps, Lexington, Kentucky, USA). One trap was deployed on each transect. Traps were suspended from the canopy, open to all directions, and sampled an area ~1.5 to 2.5 m above the forest floor. Traps were outfitted top and bottom with 1-L collection jars which were retrieved every three days or immediately after rainfall. Araneid spiders were collected along each transect at each site. Araneids that weave large, strong, vertical orb-webs in the riparian canopy were selected as representative spider predators because they consume both aquatic and terrestrial prey (Kato et al. 2004) and were distributed from the shoreline

through upland forested habitats. Araneids (mainly in the genera *Araneus*, *Eustala*, *Gasteracantha*, and *Neoscona*) at Lake Hartwell are nocturnal predators and were collected at night by hand directly from webs.

Chironomid samples were composited from thousands of individual insects. *Hexagenia* samples were composites of several individuals. Canopy trap samples from the high-PCB site were identified to family and classified into predator, herbivore, and omnivore feeding guilds (Marshall 2006) and composited into PCB samples by guild ($n = 3$) to assess trophic patterns. Terrestrial insects from the mid-PCB site were consolidated across traps and divided into replicates ($n = 3$) to assess terrestrial insect PCB load variability. Terrestrial insects from each trap at the low-PCB site were composited and analyzed separately ($n = 5$) to assess spatial patterns. At least five individual araneids were composited for each PCB sample, and at least three replicate PCB and isotope samples were analyzed per taxa, transect, or sample. Stable isotope samples of terrestrial insects consisted of individuals or composites of three or more individuals depending on size, for each taxon. All tissue samples were frozen for transport and storage prior to PCB and stable isotope analysis.

PCBs were analyzed by gas chromatography-electron capture detection (GC-ECD, Agilent 6890; Agilent Technologies, Santa Clara, California, USA) following a modified EPA method 8082 (U.S. Environmental Protection Agency 1996). This method quantifies 126 GC peaks representing 141 congeners. These were summed to calculate total PCBs. Minimum detection limits ranged from 0.167 to 8.832 ng/g among congeners. Analyte occurrence was confirmed using an alternate column, and analytes had to occur on both columns to be reported as present. Reported values were determined through the following protocol:

1) If values from both columns had <50% relative percent difference (RPD), then mean of the two values was reported.

2) If RPD >50%, then

    a) if one column had quality control (QC) problems, then data reported from the other column,

    b) if QC was similar between the columns, then lower value reported. Laboratory fortified blanks (LFBs) were analyzed twice per batch to assess accuracy and reproducibility (the relative percent difference [RPD] between two LFBs).

Recovery of LFBs averaged 91% ($\pm11\%$) and RPD averaged 6.0% ($\pm 3.9\%$) among all congeners. Method efficiency and accuracy was monitored in each sample by calculating recovery of three surrogates, PCB 34, 104, and 112, added prior to extraction. Surrogate recoveries averaged 92% ($\pm 9\%$). Three additional surrogate standards, PCB 96, 103, and 166, were added following extraction but prior to acid cleanup, to check for loss due to acid cleanup, blow down, and injection. Percent recovery of these surrogates was 93% ($\pm 10\%$).

Stable isotope ratios of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) were measured to assess spider reliance on aquatic and terrestrial prey and insect trophic position. Samples were prepared for analysis by freeze-drying and grinding to a fine powder with a ball mill or mortar and pestle. Samples were combusted to CO_2 and N_2 and analyzed in a Carlo Erba NA 1500 CHN analyzer (Carlo Erba Instrumentazione, Milan, Italy) connected to a Finnigan Delta C isotope ratio mass spectrometer (Thermo Electron, Waltham, Massachusetts, USA) to determine $\delta^{13}C$ and $\delta^{15}N$. Reference standards were PeeDee Belemnite Carbonate for $\delta^{13}C$, and nitrogen in air for $\delta^{15}N$. Reproducibility was monitored as the precision of bovine liver (National Institute of Standards and Technology No. 1577b) and an internal laboratory standard consisting of tulip poplar (*Liriodendron tulipifera*) leaves. Precision was less than one standard deviation (0.24‰ and 0.32‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively).

Analysis of variance (ANOVA) with post hoc Tukey's test was used to test for differences in PCB concentrations and isotopic signatures (using replicate isotope samples of one to three per family) between aquatic and terrestrial taxa or guilds. We estimated aquatic and terrestrial source proportions of spider prey with a single isotope ($\delta^{13}C$) mixing model using two sources: adult chironomids and terrestrial insects (Phillips and Gregg 2001). Data for chironomids and araneids were pooled among sites and sample locations; all terrestrial insect data were pooled. We excluded aquatic insect larvae from the analysis in order to avoid the potential confounding effects of metamorphosis on isotopic signature fractionation (Mihuc and Toetz 1994, Tibbets et al. 2008), and excluded *Hexagenia* because a hatch was in progress at one site only. We assumed one trophic level between insects and spiders, and corrected spider $\delta^{13}C$ for trophic fractionation using a value of 0.4‰ (Post 2002). We calculated prey source proportions for spiders at 0 m and 30 m only, because mean $\delta^{13}C$ values for araneids at 5, 10, 20, and 30 m were not significantly different.

PCB export by chironomids was estimated for the contaminated Twelvemile Creek arm of Lake Hartwell. Area of the contaminated reach was measured using ArcGIS 9.3 (ESRI, Redlands, California, USA). Mean chironomid production was estimated from the mean of comparable lakes, excluding sewage lagoons, the Great Lakes, rivers, estuaries, and outlying high and low values (15.7 ± 9.3 g·m^2·yr^{-1}, $n = 6$, Menzie 1980). Mean Lake Hartwell chironomid PCB concentration was based on samples collected offshore of our three sites, as well as eight additional sites in the contaminated arm (1324 ± 499 ng/g, $n = 40$, Walters et al. 2010).

RESULTS

The $\delta^{13}C$ and $\delta^{15}N$ signatures differed greatly between terrestrial and aquatic prey items, ($P < 0.001$, and $P < 0.001$, respectively). $\delta^{13}C$ of aquatic insects (including

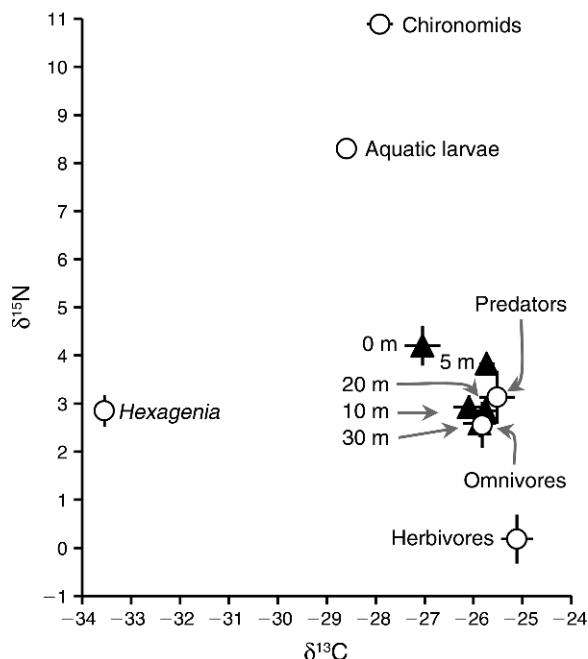FIG. 1. The δ¹³C and δ¹⁵N values (mean ± SE) for Lake
Hartwell (South Carolina, USA) food webs at the high-, mid-,
and low-PCB sites. Circles represent insects (chironomids,
Hexagenia sp., larval aquatic insects, terrestrial insect preda-
tors, terrestrial insect omnivores, terrestrial insect herbivores);
triangles represent araneid spiders (labels are distance from
shore).

larvae, −28.6‰ ± 0.9‰ [mean ± SD], $n = 27$; adult
Hexagenia, −33.6‰ ± 1.7‰, $n = 6$; and adult
Chironomidae, −27.9‰ ± 0.9‰, $n = 9$) were depleted
compared to terrestrial insects (−25.4‰ ± 1.6‰, $n = 86$,
Fig. 1). δ¹⁵N of aquatic insects (including larvae, 8.3‰
± 1.0‰, $n = 27$; adult *Hexagenia*, 2.9‰ ± 0.3‰, $n = 6$;
and adult Chironomidae, 10.9‰ ± 0.7‰, $n = 9$) were
enriched compared to terrestrial insects (1.7‰ ± 2.7‰,
$n = 86$, Fig. 1). δ¹⁵N differed among terrestrial insect
guilds ($P < 0.0001$), with predators (3.1‰ ± 2.6‰) and
omnivores (2.6‰ ± 1.3‰) enriched relative to herbi-
vores (0.2‰ ± 2.4‰, Fig. 1). Araneids became enriched
in δ¹³C and depleted in δ¹⁵N with distance inland ($P =
0.001$ and 0.006, respectively), indicating greater con-
sumption of aquatic insects prey by spiders at the
shoreline compared with populations further from
shore. The mixing model estimated 82% ± 9.6% (mean
± SE, range 62–100%) aquatic prey consumption by
araneids at the shoreline and 30% ± 6.0% (range 17–
42%) aquatic prey consumption at 30 m. However, while
shoreline araneid δ¹³C was different than terrestrial
insect δ¹³C ($P = 0.008$), araneid δ¹³C at 5, 10, 20, and 30
m were not ($P = 0.973$, $P = 0.688$, $P = 0.911$, and $P =
0.984$, respectively).
Emergent aquatic insects were more contaminated
than terrestrial insects, with Chironomidae and
Hexagenia (collected on the shoreline of the high-PCB
site only) having very high PCB levels (1675 ± 394 ng/g

[mean ± SD], $n = 8$, and 6439 ± 421 ng/g, $n = 3$;
respectively, Fig. 2) compared to terrestrial insect
predators, omnivores, and herbivores at the high-PCB
site (149 ng/g, 4 ng/g, and 3 ng/g, respectively, each $n =
1$, Fig. 2). PCBs were very low (3.1 ± 3.3 ng/g, Fig. 2) in
terrestrial insects averaged across transects at the low-
PCB site (0 m, 4 ng/g; 5 m, 8 ng/g; 10 m, 0 ng/g; 20 m,
3 ng/g; 30 m, 0 ng/g), and were not detectable in
composite terrestrial insect samples from the mid-PCB
site. Araneids on the shoreline were highly contaminated
(e.g., high-PCB site: 2436–7931 ng/g, mean = 4222 ±
2184 ng/g, $n = 5$). Araneid PCB levels corresponded to
the in-lake sediment PCB gradient ($P = 0.045$), but adult
chironomid contamination did not ($P = 0.275$, Fig. 2; see
Walters et al. 2010 for discussion of longitudinal
patterns). At the high-PCB site, terrestrial insect
predators were 37 times, midges 414 times, araneids
1206 times, and *Hexagenia* 1840 times more contami-
nated than non-predatory terrestrial insects. Insect
predator biomass at the high-PCB site was dominated
spatially by captures at 30 m (47%) and 5 m (36%), and
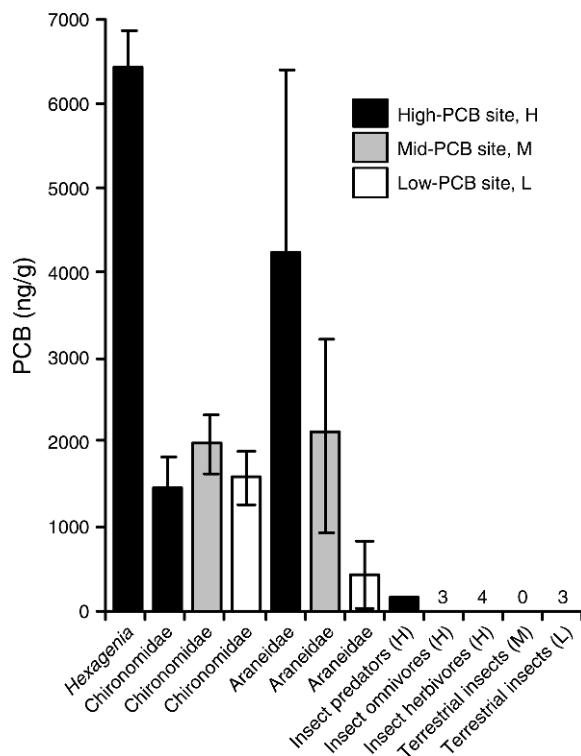taxonomically by social wasps (Vespidae, 67%).

FIG. 2. PCB concentration (ng/g wet mass) in the emergent
(adult) aquatic insects *Hexagenia* sp. (mayflies, $n = 3$),
Chironomidae (midges, $n = 8$), terrestrial Araneidae (spiders
on the shoreline, high-PCB site $n = 5$, mid- and low-PCB sites $n
= 3$), consolidated samples of multiple terrestrial insect species
from the high-PCB site ($n = 1$ for each guild; H), mean of all
terrestrial insects from the mid-PCB site ($n = 3$; M), and mean
of all traps from the low-PCB site ($n = 5$; L). Error bars are
±SD. Numbers indicate mean PCB concentrations not visible
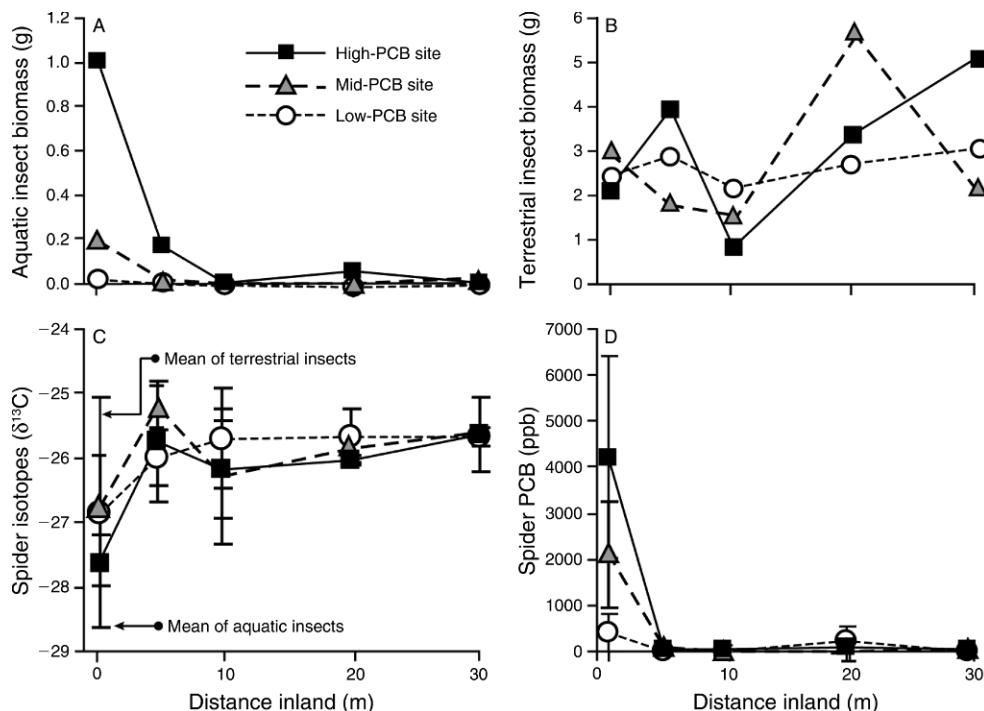as illustrated.

FIG. 3.   Spatial patterns of occurrence, isotopes, and contamination in predators and prey in the riparian zone of Lake Hartwell at the high-, mid-, and low-PCB sites. (A) Emergent aquatic insect availability. (B) Terrestrial insect availability. (C) Mean (±SD) carbon stable isotopes in araneid spiders and insect prey. (D) Mean (±SD) PCB concentrationsm in araneid spiders.

Terrestrial insect predators from the high-PCB site were more contaminated than araneids pooled from all transects ≥5 m from the shore at the high-PCB site (58 ± 19 ng/g).

Aquatic insect prey availability, spider consumption of aquatic prey, and spider PCB concentrations were greatest at the shoreline and declined inland as expected. Aquatic insect biomass declined rapidly inland ($P = 0.008$) and was negligible beyond 5 m (Fig. 3A). Aquatic insect prey availability and spider PCBs declined inland at a negative exponential rate with distance from shore ($y = ae^{-bx}$, where $a = 1.35$ and $b = 0.31$ for insect abundance, and $a = 2.00$ and $b = 0.69$ for PCBs). Terrestrial insect biomass, generally 4–10 times that of aquatics, was invariant with distance ($P = 0.501$, Fig. 3B). Araneid $\delta^{13}C$ became more enriched ($P = 0.001$, Fig. 3C) with distance inland, reaching an asymptote by 5 m to within <1‰ of terrestrial insects. Araneid PCB concentrations were greatest at the shoreline and decreased rapidly inland at the high, mid and low-PCB sites ($P = 0.038$, $P = 0.034$, $P = 0.038$, respectively; Fig. 3D). Based on lake area, literature-derived production estimates, and measured PCB concentration data, chironomids export an estimated 41 ± 29 g PCB/yr to the Lake Hartwell riparian zone.

DISCUSSION

The mechanism of contaminant transfer from aquatic sediments to terrestrial invertebrate predators through consumption of emergent aquatic insects was supported by multiple lines of evidence that confirmed a priori predictions. This demonstrated the importance of ecological subsidy as a mechanism of contaminant exposure in terrestrial insectivores relative to alternative processes, such as direct acquisition by terrestrial insects from soils (Heikens et al. 2001). Isotopes, prey availability, and PCBs indicated transfer of aquatic sediment-derived PCBs to terrestrial food webs through consumption of emergent aquatic insects. Corroboration between these variables was possible due to divergent aquatic and terrestrial signals. For example, a strong pattern was present in spider carbon isotopes with distance inland.

Shoreline spider carbon isotopes were depleted, indicating increased reliance on aquatic prey relative to inland spiders. Araneid carbon enrichment with distance from shore was consistent with slight carbon fractionation in spiders relative to prey (Oelbermann and Sechu 2002) and observed differential aquatic and terrestrial carbon isotope signals. Observed terrestrial insect $\delta^{13}C$ was consistent with $\delta^{13}C$ observed in other riparian zones (Akamatsu et al. 2004), and not significantly different than carbon isotopes in spiders ≥5 m inland. Mixing model analysis indicated that shoreline araneids consumed 82% aquatic prey, consistent with an estimate of 86% from 11 sites in the Twelvemile Creek arm of Lake Hartwell (Walters et al. 2010), whereas araneids 30 m from shore consumed 30% aquatic prey. The 30-m mixing-model estimate is at odds with observed similar-

ity of carbon signatures between terrestrial insects and spiders ≥5 m inland, measures of aquatic insect biomass, and araneid PCB concentrations. Aquatic insects were rarely collected at distances >5 m from shore. PCB concentrations were one to three orders of magnitude higher in aquatic insect than terrestrial insects, similar to the magnitude of difference between shoreline and upland spider PCB concentrations, and declined to very low levels within 5 m of shore. Hence, these lines of evidence both supported the importance of ecological subsidy to contaminant transfer and suggested that transfer was largely limited to within ~5 m of the shoreline. The conflicting estimate of 30% aquatic prey consumption at 30 m could be attributed to small differences in $\delta^{13}C$ between sources used in the mixing model. Chironomid and terrestrial insect $\delta^{13}C$ differed by 2.6‰, whereas the minimum difference among sources to be used in this model is 2‰ (Phillips and Gregg 2001). Hence, while the mechanism of exposure via consumption of aquatic prey was clearly established, high resolution of food web patterns relevant to contaminant exposures was not possible.

$\delta^{15}N$ is typically used to assess trophic position, and araneids, consistent with other predators, become enriched in nitrogen relative to prey (Oelbermann and Sechu 2002). However, interpretation of observed $\delta^{15}N$ data was confounded by highly variable enrichment of aquatic insects relative to terrestrial insects (Fig. 1), similar to patterns in other lakes and streams where $\delta^{15}N$ was used to assess aquatic resource utilization by terrestrial predators (Hebert et al. 2000, Sanzone et al. 2003, Paetzold et al. 2005). Spiders at 0 m and 5 m were enriched relative to *Hexagenia* and all terrestrial insects. Spiders further inland were not enriched relative to *Hexagenia*, but were enriched relative to the mean of terrestrial insects. Hence, nitrogen depletion in araneids with distance from shore indicated a shift to terrestrial prey. One might expect that spiders consuming aquatic prey should have been more enriched in nitrogen than observed, especially due to the presence of highly enriched chironomids. The correspondence of shoreline spider PCBs to offshore sediment PCBs rather than offshore chironomids suggests that chironomids may not have been a dominant food source for araneids. Further, *Hexagenia* were present in large numbers at the high-PCB site during sampling. *Hexagenia* hatch over a brief period, but are locally important prey because they occur in massive swarms (Corkum et al. 2006). Differential PCB uptake and isotope turnover rates could confound observation of effects from such pulsed inputs. PCB uptake rates in consumers are rapid (Fisk et al. 1998), and *Hexagenia* consumption may have contributed to PCB concentrations in araneids measured at the high-PCB site. However, slower tissue turnover for stable isotopes in spider tissue could obscure the relative importance of *Hexagenia* to shoreline araneid diet (Tieszen et al. 1983).

The alternative mechanism of consumption of terrestrial insects contaminated through exposure to PCBs from contaminated overbank deposits through terrestrial food webs was not supported. The high- and low-PCB sites were located on shores with elevations higher than the maximum elevation reached by surface waters between 1962 and 2007 (Appendix A: Fig. A2), and thus contaminated sediment could not have been deposited by flooding at these sites. It is not possible for floods to have reached the elevations of the high and low-PCB sites between 1955 (beginning of PCB discharges) and 1962 (completion of the Hartwell Dam). The mid-PCB site was located on a shore with an elevation low enough to be exposed to some high water events (Appendix A: Fig. A2). However, the mid-PCB site had moderate spider contamination levels consistent with offshore sediment contamination levels, and terrestrial insects had no detectable PCBs.

The estimated chironomid contaminant flux (41 g PCB/yr) was equivalent to PCBs delivered by 310 000 ± 220 000 (mean ± SD) returning Chinook salmon (1.3 g PCB per 10 000 fish; Compton et al. 2006), but underestimates the total amount of exported PCBs by not including other emergent insects such as mayflies and caddisflies. While this estimate was infinitesimal compared to the total PCB load delivered to the aquatic system (181 MT), the toxicity of PCBs is such that this flux results in toxicologically significant exposures. For example, the PCB concentration in the most contaminated shoreline araneids exceeded the wildlife value (WV, or concentration in prey necessary to deliver a potentially harmful dose to predators) for nestling chickadees by more than 10 times (Walters et al. 2010). These exposure levels also occurred despite Lake Hartwell having a high shoreline-to-area ratio (i.e., shoreline development factor, $D_L = 5.1$), which could dilute contaminant flux by spreading the contaminant load across a long shoreline (Gratton and Vander Zanden 2009).

Hypotheses that the spatial extent of lateral subsidy should increase in aquatic ecosystems downstream of headwaters, subject to wind advection and with greater secondary production than in headwaters (Power and Rainey 2000), were not supported. Evidence for wind advection of emergent aquatic insects was indicated by PCB levels in flying chironomids, which did not correspond spatially to in-sediment PCB levels, as opposed to sedentary spiders. Instead, contaminant flux into intact riparian forest at Lake Hartwell was largely limited to ~5 m inland. The decay rate of aquatic prey availability and PCB contamination away from the shoreline was consistent with lateral patterns of aquatic insect abundance observed in riparian zones in headwater (Sanzone et al. 2003, Briers et al. 2005) and mid-sized streams (Power et al. 2004), and was more rapid than rates observed in lakes with non-forested riparian zones (Gratton and Vander Zanden 2009). These findings among different aquatic habitats suggest that the spatial

extent of aquatic insect subsidy may be more strongly influenced by characteristics of the recipient riparian environment than by the donor aquatic system. For example, aquatic insects may fly further from shore with seasonal foliage reductions (Power and Rainey 2000), shoreline development, increasing riparian forest fragmentation, and non-forest plant communities. Artificial lights also alter aquatic insect flight behavior (Longcore and Rich 2004) and could subsequently alter spatial patterns of subsidy and contaminant transfer. Spatial patterns of material transfer may also be affected by foraging behavior. Social wasps, for example, may behave like bats, moving aquatically derived materials great distances independently of the spatial configuration of contaminant source-areas (Power et al. 2004). Indeed, the furthest sampling locations were 30 m from the shoreline, less than 1/10th the foraging distance of some Vespidae (Akre et al. 1975).

CONCLUSIONS

Walters et al. (2008) argued that persistent contaminants are underused tracers of energy flow that can be used to study trophic relationships at large spatial scales, including ecological subsidy, not physically possible through traditional tracer methods such as stable isotope enrichment. In the present study, PCBs (1) were quantifiable tracers labeling a huge area that clearly distinguished the aquatic (moderate to high PCBs) from the terrestrial signal (negligible PCBs), thus identifying food web pathways, and (2) corroborated evidence of aquatic prey reliance from prey availability and natural isotope abundances. Further, examination of PCBs allowed us to test the previously unaddressed hypothesis that aquatic subsidies from larger, productive systems should extend further into terrestrial environments. Persistent contaminants could also be used as tracers to study trophic relationships over long time periods, or as affected by land use, disturbance, climate change, or food web alteration such as biological invasion.

Consistent with historical perceptions of aquatic ecosystems as recipients of land-derived materials, lakes have been regarded as contaminant sinks (Vander Zanden and Sanzone 2004). This study contributes to changing views of land–water interaction (Gratton and Vander Zanden 2009) by documenting the spatial extent to which lakes can act as sources of contaminants to riparian food webs. This linkage occurs through the delivery of aquatic sediment-derived contaminants by emergent aquatic insects. Riparian invertebrates intercept contaminated aquatic prey and accumulate sediment-derived contaminants. These contaminants are then available to higher terrestrial predators (Cristol et al. 2008). Spiders may be most important in this regard as key predators of emergent aquatic insects (Baxter et al. 2005). We argue that insect emergence is therefore a limiting step in the process of contaminant transfer from freshwater to terrestrial ecosystems. Considering the global ubiquity of aquatic insects and widespread contamination of aquatic ecosystems, insect emergence is likely a major vector of contaminant transfer from aquatic to terrestrial food webs.

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APPENDIX A

Location of study area and sampling sites (*Ecological Archives* A021-045-A1).

APPENDIX B

Lake Hartwell water elevation 1962–2007 (*Ecological Archives* A021-045-A2).