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Riparian Spiders: Sentinels of Polychlorinated Dibenzo-*p*-dioxin and Dibenzofuran–Contaminated Sediment

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Abstract: Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) are persistent, toxic, and bioaccumulative. Currently, PCDD/F monitoring programs primarily use fish and birds with potentially large home ranges to monitor temporal trends over broad spatial scales; sentinel organisms that provide targeted sediment contaminant information across small geographic areas have yet to be developed. Riparian orb-weaving spiders, which typically have small home ranges and consume primarily adult aquatic insects, are potential PCDD/F sentinels. Recent studies have demonstrated that spider tissue concentrations indicate the source and magnitude of dioxin-like chlorinated compounds in contaminated sediments, including polychlorinated biphenyls (PCBs). Our aim in the present study was to assess the utility of riparian spiders as sentinels for PCDD/F-contaminated sediments. We measured PCDD/F (total [Σ] and homologs) in surface sediments and spiders collected from three sites within the St. Louis River basin (Minnesota and Wisconsin, USA). We then compared (1) patterns in ΣPCDD/F concentrations between sediment and spiders, (2) the distribution of homologs within sediments and spiders when pooled across sites, and (3) the relationship between sediment and spider concentrations of PCDD/F homologs across 13 stations sampled across the three sites. The ΣPCDD/F concentrations in sediment (mean ± standard error 286 591 ± 97 614 pg/g) were significantly higher than those in riparian spiders (2463 ± 977 pg/g, $p < 0.001$), but the relative abundance of homologs in sediment and spiders were not significantly different. Spider homolog concentrations were significantly and positively correlated with sediment concentrations across a gradient of sediment PCDD/F contamination ($R^2 = 0.47$, $p < 0.001$). Our results indicate that, as has been shown for other legacy organic chemicals like PCBs, riparian spiders are suitable sentinels of PCDD/F in contaminated sediment. *Environ Toxicol Chem* 2023;42:414–420.

Keywords: Dioxins; furans; fate and transport; sediment chemistry

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) are persistent and toxic, and they bioaccumulate in fatty tissues (Lallas, 2001). PCDD/F contaminated sediment can result from combustion processes and historical industrial activity (Kanan & Samara, 2018; Lorber et al., 2013; Tuchman et al., 2018). Sediments contaminated with PCDD/F are the source of PCDD/F uptake in aquatic food webs, which can culminate in harmful exposure to humans via wildlife fish consumption. Concerns over health risks from these exposures have resulted in the issuance of fish consumption advisories, the implementation of costly remediation projects to mitigate exposure risks (Cornelissen et al., 2012; Richman et al., 2016), and the initiation of extensive monitoring studies to track PCDD/F in the environment (Gandhi et al., 2019; Turyk et al., 2012; White & Birnbaum, 2009).

One approach to monitoring PCDD/F contamination includes the use of sentinel organisms, hereafter *sentinels*—biological monitors that accumulate contaminants in their tissues without significant adverse effects (Beeby, 2001). To date, most proposed PCDD/F sentinels either (1) monitor atmospheric deposition via plankton (Morales et al., 2015) or plants, (i.e., moss or spruce/pine needles; Carballeira et al., 2006; Holt et al., 2016; Zhu et al., 2007); (2) monitor local contamination

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using birds such as tree swallows (*Tachycineta bicolor*), which forage within 1 km of their nest sites, or blue tits (*Cyanistes caeruleus*; Custer, 2011); or (3) monitor temporal trends via animals that integrate the contaminant signal over a broader spatial scale such as guillemot (*Uria aalge*) or gull (*Larus michahellis*) eggs (Miller et al., 2014; Morales et al., 2016) or sport fish (Falk et al., 1999; Gandhi et al., 2019; Turyk et al., 2006). Recently, Gandhi et al. (2019) suggested that fish, sentinels with large home ranges, limited the efficacy of comprehensive monitoring programs and that these programs can be replaced with the monitoring of targeted/local PCDD/F contamination using sentinels.

Riparian orb-weaving spiders (Tetragnathidae and Araneidae) are potential sentinels for local PCDD/F contamination. These spiders are broadly distributed, feed primarily on adult aquatic insects, and have been utilized as sentinels of sediments contaminated with dioxin-like chlorinated compounds, like polychlorinated biphenyls (PCBs; Kraus et al., 2017; Walters et al., 2008, 2010, 2018) and other persistent aquatic pollutants such as mercury and selenium (Chumchal et al., 2022). Spider PCB concentrations have demonstrated forensic applications via PCB homolog source tracking (Walters et al., 2018), and their tissues have correlated with sediment contamination at small spatial scales—tens to hundreds of meters (Walters et al., 2010). To date, no studies have tested the effectiveness of riparian spiders integrating sediment PCDD/F contaminant signal in their tissues (Chumchal et al., 2022).

In the present study, our overall aim was to assess the utility of riparian spiders as sentinels of PCDD/F-contaminated sediments at three sites (13 sampling stations) located within the St. Louis River basin of Lake Superior (Minnesota and Wisconsin, USA). We analyzed PCDD/F homologs (tetra-, penta-, hexa-, and hepta-Cl homologs) as well as the fully chlorinated octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF) compounds (hereafter collectively referred to as *homologs*) in surface sediment and spider tissues. In the present study, we first characterized and compared ΣPCDD/F concentrations (sum of all homologs) in surface sediment and riparian spider tissues. We then tested if PCDD/F homolog distributions within riparian spider tissues tracked those measured in sediments. Finally, we investigated whether PCDD/F homolog concentrations in spiders varied predictably along a gradient of PCDD/F contamination in sediments that we observed across sampling stations.

MATERIAL AND METHODS

Site description and sample collection

The St. Louis River forms the geographic boundary between Minnesota and Wisconsin and is the largest US tributary to Lake Superior. Historically, the St. Louis River has provided regional shipping access to Lake Superior, and development and industrial activity along the St. Louis River over the past 130 years has resulted in contaminated sediments in some locations (Stine, 2013). This resulted in the lower 63 km of the St. Louis River, from upstream of Cloquet, Minnesota, to its mouth at the Duluth/Superior Harbor, as well as other portions of the watershed to be designated an area of concern under the Great Lakes Water Quality Agreement (Governments of Canada and the United States, 1972; Supporting Information, Figure S1). Surface sediment and spiders were collected from three sites within the St. Louis River area of concern: Scanlon and Thomson reservoirs in August 2017 and Ponds behind Erie Pier in August 2019. Surface sediment was collected from five stations at Scanlon and Thomson reservoirs. Surface sediment was collected from four stations at Ponds behind Erie Pier; however, owing to low spider biomass, surface sediment concentrations measured at two neighboring Ponds behind Erie Pier stations were averaged to facilitate a comparison with spiders collected from the neighboring shoreline (Ponds behind Erie Pier stations = 3). Spiders were collected from shoreline adjacent to surface sediment stations at night from a boat or via wading. Spider sampling methodologies among the sites were identical with one exception. Tetragnathids (Tetragnathidae) and araneids (Araneidae) were combined in a mixed taxa composite at Scanlon and Thomson reservoirs; only tetragnathid spiders were sampled at Ponds behind Erie Pier owing to low araneid biomass. Surface sediment (top 15 cm), hereafter referred to as *sediment*, was collected once at each station; and one to three replicate composite samples of spiders were collected depending on local biomass. Maps, station localities, and additional details on sediment and spider sampling are provided in Supporting Information, Figures S2–S4.

PCDD/F analysis

Sediment and spider samples were analyzed for dioxins and furans using high-resolution gas chromatography/mass spectrometry via US Environmental Protection Agency (USEPA) Method 1613B (USEPA, 1994). Samples were extracted in Soxhlets with hexane and dichloromethane for 16 h, followed by acid washing and silica gel column cleanup. Extracts were concentrated using a rotary evaporator and then prepared by adding 20 µl of a nonane solution containing 100 pg/µl of the recovery standards. A 1-µl aliquot of the concentrated extract was injected into the system, capable of performing selected ion monitoring at resolving powers of at least 10,000 (10% valley definition). Quality assurance and quality control data are summarized in the Supporting Information.

Total organic carbon and lipid analysis

Total organic carbon is a measure of the total amount of nonvolatile, partially volatile, and particulate organic compounds in a sample. Sediment total organic content analysis was performed according to USEPA Method 9060 (USEPA, 2004). Sediment samples were acidified to remove inorganic carbon (carbonates, bicarbonates, free carbon dioxide [CO_2], etc.) and then combusted in a high-temperature furnace in an oxygen atmosphere to convert organic and inorganic forms of carbon to CO_2. Combustion product gases were swept through a barium chromate catalyst/scrubber to ensure that all carbon was oxidized to CO_2. The gas stream was passed to a coulometer cell filled with a partially aqueous

medium containing ethanolamine and a colorimetric indicator. Then, CO_2 was measured with an infrared detector and reported as percentage of carbon on a dry weight basis.

Lipid content (as total extractable organics) in tissue was determined gravimetrically. An aliquot of prealumina sample extract from the PCDD/F solvent extraction was dried at 40 °C until all solvent evaporated. Percentage of lipid was then determined by a gravimetric analysis of extract residue after the solvent evaporated. Results were reported as percentage of lipids on a wet weight basis.

Data analysis

Only values detected at concentrations above the method detection limits were considered. Sediment homolog concentrations were total organic carbon–normalized, and spider homolog concentrations were lipid-normalized within each sample. The arithmetic mean was then calculated for each homolog across replicates within each station, producing a mean sediment concentration and mean spider concentration for each station. These station profiles were treated as independent replicates during further analyses, and all analyses used an α value = 0.05 to determine significance. Data analyses were conducted in R (Ver 4.1.3, and R Studio, Ver 1.4.1106-5).

Our initial analysis was to determine if (1) there were differences among sites for either sediment or spider ΣPCDD/F, and if (2) there were differences between sediment and spider ΣPCDD/F within each site. Concentrations of ΣPCDD/F were calculated at each sampling station as the sum of the tetra-, penta-, hexa-, and hepta-Cl homologs as well as the fully chlorinated OCDD and OCDF compounds. Sediment and spider ΣPCDD/F were $\log_{10}$-transformed to reduce the skewedness of the data. Sediment and spider $\log_{10}$-transformed ΣPCDD/F were analyzed for normality using a Shapiro-Wilks test (sediment $p = 0.67$, spiders $p = 0.21$) and for equal variance using Levene's test (sediment $p = 0.82$, spiders $p = 0.45$). Differences in $\log_{10}$-transformed sediment and spider total PCDD/F among sites were then investigated using one-way analysis of variance (ANOVA) with site as a fixed effect. Differences between $\log_{10}$-transformed sediment and spider total PCDD/F concentrations were investigated using one-way ANOVAs with matrix (i.e., spider and sediment) as a fixed effect.

We then tested if PCDD/F homolog profiles—the distribution of PCDD/F homologs—observed within riparian spider tissues tracked those measured in sediments. For the present analysis, we tested whether PCDD/F homolog profiles differed within sediment and spiders among sites and whether PCDD/F profiles differed between sediments and spiders within each site. We compared two profiles: contaminant concentrations and relative abundance of homologs. Relative abundance was calculated by dividing each homolog concentration (pg/g) by the sum of all homolog concentrations (pg/g) for each replicate. The Kolmogorov-Smirnoff two-sample distribution test was used to compare homolog profiles using the ks.boot() function of the Matching package (Sekhon, 2011) with default settings.

Finally, we used analysis of covariance (ANCOVA) to test if spider PCDD/F homolog concentrations tracked homolog concentrations in sediments measured across all sampling stations. The ANCOVA model included sediment concentration as a covariate and homolog group as a fixed effect on spider concentrations. Sediment and spider contaminant concentrations were $\log_{10}$-transformed prior to analysis to reduce the skewedness of the data. A full-factorial model was used to investigate whether the relationship between sediment homolog concentrations and spider homolog concentrations varied between homolog groups. We included all available data points in our final analysis ($n = 58$ sediment vs. spider concentrations across 13 stations). Tetrachlorodibenzo-*p*-dioxin (TCDD) and pentachlorodibenzo-*p*-dioxin were never detected at a quantifiable level in spiders (i.e., an unknown number below our detection limit but not 0) and were not considered for this analysis. Model details are provided in the Supporting Information. All raw data and associated method detection limits are provided as Supporting Information (see Sediment and Spider PCDDF Raw Data Supplement). Paired sediment and spider data are provided as Supporting Information (see Sediment and Spider PCDDF Paired Data Supplement).

RESULTS

∑PCDD/F in sediments and spiders

Total PCDD/F concentrations among the 13 sampling stations ranged from 38,167 to 1,295,149 pg/g (mean ± standard error [SE] = 286,591 ± 97,614 pg/g) in sediments and from 179 to 9608 pg/g (2463 ± 977 pg/g) in riparian spiders collected from the adjacent shoreline (Figure 1). The sum of PCDD/F concentrations were not significantly different among study sites for sediments (ANOVA, $F_{2,10} = 1.28$, $p = 0.32$) or spiders (ANOVA, $F_{2,10} = 0.21$, $p = 0.82$). Mean concentration of ΣPCDD/F in sediments were one to three orders of magnitude higher than in spiders (ANOVA, $F_{1,24} = 107.1$, $p < 0.001$). Overall, sediment concentrations were similar among study sites (Supporting Information, Figure S7), and spider tissue concentrations were consistently and significantly lower than site sediment.

∑PCDD/F homolog distribution and concentrations in sediments and spiders

Neither homolog concentrations nor relative abundance profiles were different among study sites for sediments or spiders (Supporting Information, Table S1, all p values > 0.05). Homolog concentrations of sediments were consistently higher than those of spiders by two to three orders of magnitude within sites (Supporting Information, Figure S7, all p values < 0.05). However, the relative abundance of homolog concentrations was not different between sediments and spiders within each site (all p values > 0.05; site comparisons presented in Supporting Information, Figure S8 and summarized in Figure 2). Thus, while spider concentrations were substantially lower than sediment concentrations for ΣPCDD/F

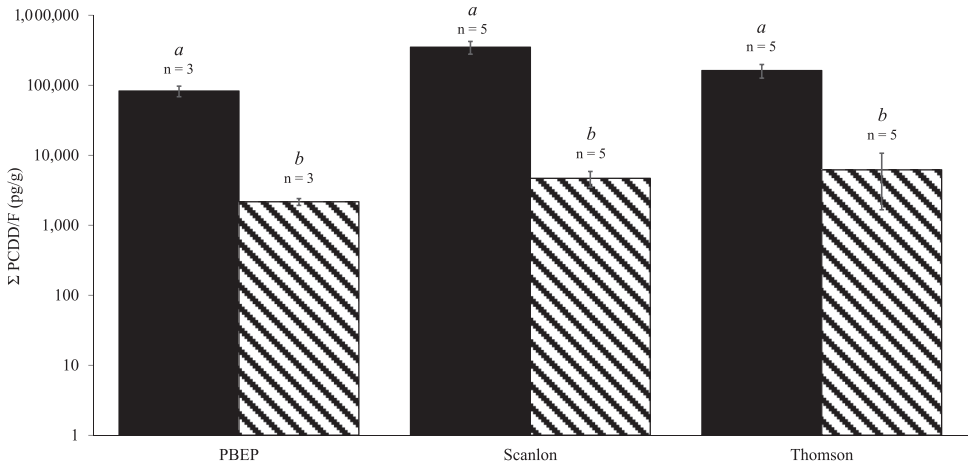

FIGURE 1: Mean ± standard error of total polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) concentrations (pg/g) in total organic carbon–normalized sediment (black bars) and lipid-normalized spiders (hatched bars) collected at Ponds behind Erie Pier, Scanlon Reservoir, and Thomson Reservoir. Sample sizes of each matrix (sediment and spiders) collected from each site are shown above the respective bar. Connecting letters indicate differences among site × matrix. PBEP = Ponds behind Erie Pier.

(Figure 1) and individual homologs, the relative abundance of homologs in spider tissues tracked those measured in sediments (Figure 2).

We investigated the relationship between all paired spider tissue and sediment homolog concentrations across sites and stations ($n = 58$). We found that homolog concentrations in spider tissues were significantly and positively correlated with those in sediment (y-int ± SE = –0.514 ± 0.592 $\log_{10}$[(pg spider] slope ± SE = 0.682 ± 0.135 $\log_{10}$[pg spider]/$\log_{10}$[pg sediment]; $F_{1,57} = 53.9$, $p < 0.001$, $R^2 = 0.57$); however, there was no effect of homolog group ($F_{1,7} = 1.7$, $p = 0.127$). These results indicate that if sediment concentrations of the different homologs were similar, spider contaminant concentrations of those same homologs were also similar (Figure 3).

DISCUSSION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are among the most persistent and toxic contaminants on Earth (Lallas, 2001). Although some organisms such as birds and fishes have been used as sentinels of PCDD/F exposure at larger spatial scales, sentinels at finer spatial scales are lacking. An effective fine-scale sentinel requires a defined route of exposure, insensitivity to the pollutant, and tissue concentrations that correspond to ambient concentrations consistently across space and time (Beeby, 2001). The tetragnathid and araneids collected in the present study have high proportions of adult aquatic insects in their diet (Akamatsu & Toda, 2011; Jackson et al., 2021; Raikow et al., 2011); have historically been found near areas with high levels of persistent contaminants, with no observed adverse effects (Chumchal et al., 2022); and integrate contaminant signals at small spatial scales (<100 m) for a wide variety of organic contaminants including PCBs, per- and polyfluoroalkyl substances, pharmaceuticals, and endocrine disruptors (Koch et al., 2021; Previšić et al., 2021; Richmond et al., 2018; Walters et al., 2008). We demonstrated that spider tissues reflect sediment PCDD/F homolog distributions as well as homolog concentrations along a PCDD/F homolog contamination gradient. This extends the utility of riparian spiders as sentinels of aquatic contamination to a new class of compounds that had not been previously considered (Chumchal et al., 2022).

Sediment ΣPCDD/F concentrations were not different among sites and were consistently two orders of magnitude greater than those of spiders. The low concentrations in spiders relative to sediment may be attributable to low bioavailability (Alexander, 2000; Lyytikäinen et al., 2003; Van Geest et al., 2011), high metabolic transformation rates leading to trophic dilution (Walters et al., 2016; Wan et al., 2005; Zhu et al., 2015), or low metamorphic retention in adult aquatic insects. One study did find high metamorphic retention in 2,3,7,8-TCDD (West et al., 1997); but metamorphic retention rates have not been measured for the more rapidly metabolized homologs considered in the present study. The mechanism(s) driving the attenuation of the "sediment to spider signal" ultimately did not affect the validation of spiders as a PCDD/F sentinel because spider tissues still tracked (1) homolog distribution profiles within each respective site, and (2) the magnitude of contamination across a PCDD/F concentration gradient. These results indicate that riparian spiders may be a suitable sentinel for other previously unstudied contaminants that have a low probability of trophic magnification but are robustly characterized as homologs/congeners (e.g., polybrominated diphenyl ethers) or across a broad class of compounds (e.g., polycyclic aromatic hydrocarbons).

Relative abundance profiles can be used to differentiate between different PCDD/F sources (see Sundqvist et al., 2009). However, it is noteworthy that sediment profiles observed in the present study were not different among sites, so future work is needed to explicitly test source discrimination. Walters et al. (2018) used riparian spider PCB homolog profiles to differentiate sources of PCBs within a large contaminated sediment site. We found that spider homolog profiles were conserved relative to those in sediment, suggesting that they have utility for PCDD/F source tracking.

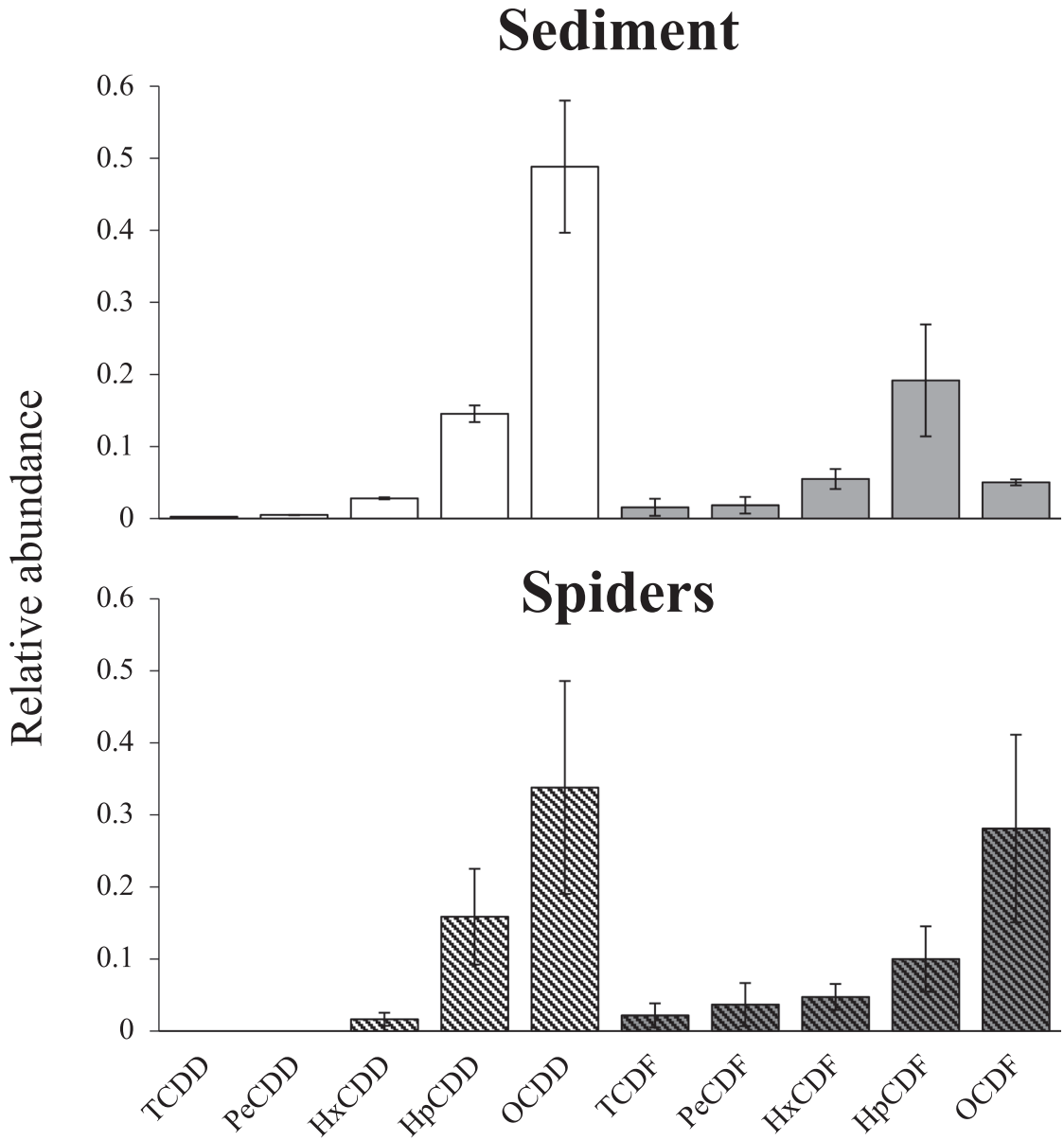

FIGURE 2: Surface sediment and spider mean ± standard error relative abundance for polychlorinated dibenzo-*p*-dioxin (white) and polychlorinated dibenzofuran (gray) homologs. Values are pooled among sites. TCDD = tetrachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octachlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran.

One limitation of spiders as sentinels of organic contaminants is their small body size. Multitaxa composites may be necessary to increase sample mass and to reduce the method detection limits of the toxic 2,3,7,8-Cl substituted congeners. Congener data not only may assist source tracking via the comparison of more robust congener profiles (i.e., profiles include 15 congeners as opposed to, or in addition to, 10 homologs) but also would allow the modeling of dietary exposure to passerine birds via the spider exposure pathway (Beaubien et al., 2020). In the present study we composited tetragnathids and araneids whenever possible to achieve greater sample mass for chemical analyses. Spider ΣPCDD/F concentrations and relative abundance profiles were not statistically different among sites, suggesting that multitaxa composites were appropriate. However, intertaxa comparisons of tetragnathids and araneids have been reported for dioxin-like compounds, like PCBs, but with mixed results. PCB concentrations in tetragnathids have been reported as higher than (Walters et al., 2018), equivalent to (Kraus et al., 2017), and lower than (Walters et al., 2010) concentrations in araneids. More research would help explain the assumptions of multitaxa compositing techniques for organic contaminants with high mass requirements like PCDD/F. Future research could include web-building taxa collected in the present study (tetragnathids and araneids), other prominent riparian taxa like fishing spiders (Pisauridae), and

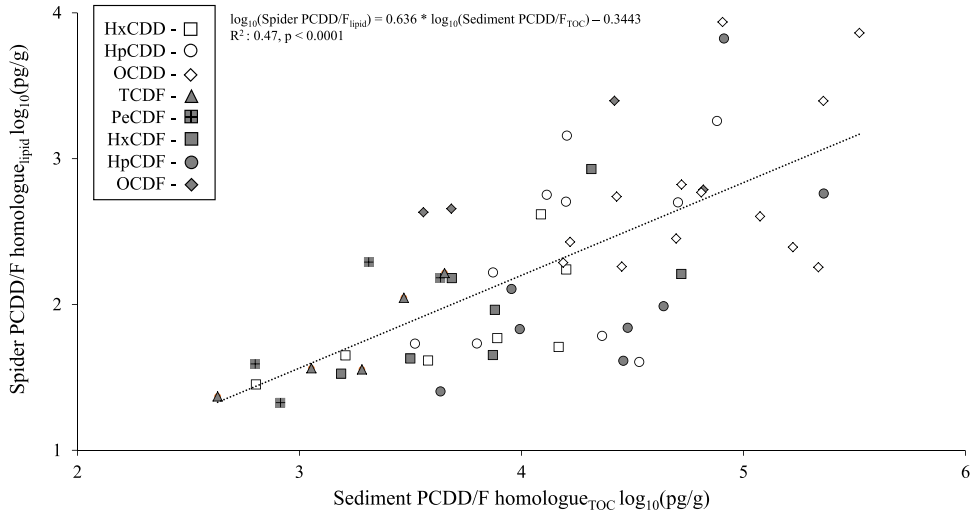

FIGURE 3: Relationship between polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran homologs in sediment and spiders. Each point represents the station mean total organic carbon (TOC)–normalized sediment concentration and station mean lipid-normalized spider concentration for each homolog. PCDD/F = polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octachlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran.

any other spider capturing aquatic prey found within a meter of the shoreline.

Supporting Information—The Supporting Information is available on the Wiley Online Library at https://10.1002/etc.5531.

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Data Availability Statement—All data may be found online in the Supporting Information.

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