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# PCB concentrations in riparian spiders (Tetragnathidae) consistently reflect concentrations in water and aquatic macroinvertebrates, but not sediment: Analysis of a seven-year field study

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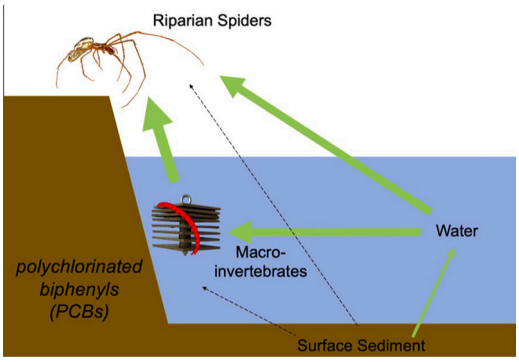
## HIGHLIGHTS

- Tetragnathid spiders are sentinels for PCB pollution in rivers.
- PCB concentration in spiders consistently predicted those in river insects and water.
- PCB concentrations in spiders did not predict those in river sediments.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Tetragnathid spiders have been used as sentinels to study the biotransport of contaminants between aquatic and terrestrial environments because a significant proportion of their diet consists of adult aquatic insects. A key knowledge gap in assessing tetragnathid spiders as sentinels is understanding the consistency of the year-to-year relationship between contaminant concentrations in spiders and sediment, water, and macroinvertebrates. We collected five years of data over a seven-year investigation at a PCB contaminated-sediment site to investigate if concentrations in spiders were consistently correlated with concentrations in sediment, water, and aquatic macroinvertebrates. Despite significant year-to-year variability in spider PCB concentrations, they were not correlated with sediment concentrations ($p = 0.186$). However, spider PCB concentrations were significantly, positively correlated with PCB concentrations in water ($p < 0.0001$, annual $r^2 = 0.35–0.84$) and macroinvertebrates ($p < 0.0001$; annual $r^2 = 0.59–0.71$). Analysis of covariance (ANCOVA) showed that spider PCB concentrations varied consistently with water ($\beta = 0.63$) and macroinvertebrate PCB concentrations ($\beta = 1.023$)

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among years. Overall, this study filled a critical knowledge gap in the utilization of tetragnathid spiders as sentinels of aquatic pollution by showing that despite year-to-year changes in PCB concentrations across environmental compartments, consistent relationships existed between spiders and water and aquatic macroinvertebrates.

## 1. Introduction

Contamination of aquatic sediment in freshwater ecosystems is a global environmental problem. While efforts to remediate contaminated sediment are largely motivated by well-characterized risks to aquatic environments (e.g., National Research Council, 2001), freshwater and terrestrial ecosystems are tightly linked by cross-system fluxes of elements, organic matter, and animals, particularly merolimnic insects (Baxter et al., 2005; Schulz et al., 2015; Schulz and Bundschuh, 2020). Larval aquatic insects can accumulate contaminants and then transport them to land when they emerge as adult aquatic insects (Kraus, 2019; Otter et al., 2020; Walters et al., 2020; Kraus et al., 2021). Adult aquatic insects are important prey for many consumers on land such as birds, spiders, and bats, so the associated environmental risks of contaminated aquatic sediment may also propagate to terrestrial food webs and ecosystems (Custer et al., 2005; Walters et al., 2008; O'Shea and Johnston, 2009).

Riparian spiders have been used as sentinels of aquatic contamination, in part because a significant proportion of their diet consists of adult aquatic insects (Otter et al., 2013; Tweedy et al., 2013; Gann et al., 2015; Kraus et al., 2017; Walters et al., 2018). Many of these studies focus on spiders in the family Tetragnathidae (Otter et al., 2013; Walters et al., 2018; Beaubien et al., 2019), as most members of this family are specialized predators on adult aquatic insects and are obligate riparian species with a near-global distribution (Walters et al., 2010; Chumchal et al., 2022). For example, Tweedy et al. (2013) showed a significant correlation between methyl mercury concentrations in emergent insects (chironomids and caddisflies) and tetragnathid spiders in experimental ponds. Contaminant concentrations in tetragnathid spiders also correlate well with surface sediment concentrations adjacent to their riparian habitat. Both Walters et al. (2010) and Kraus et al. (2017) showed significant relationships between sediment concentrations of polychlorinated biphenyls (PCBs) and tetragnathid spiders at Lake Hartwell (South Carolina, USA) and Manistique River (Michigan, USA), respectively.

One key knowledge gap in the assessment of tetragnathid spiders as sentinels is the consistency of the year-to-year relationship that exists between spider contaminant concentrations and abiotic (sediment and/or water) and other biotic (macroinvertebrates) endpoints (Chumchal et al., 2022). Existing studies have focused on the relationship between contaminant concentrations in tetragnathid spiders and other endpoints during a single field sampling event or season (Walters et al., 2010; Otter et al., 2013; Tweedy et al., 2013).

In the present study, we investigate if PCB concentrations in tetragnathid spiders were consistently correlated with PCB concentrations in sediment, water, and aquatic macroinvertebrates. This study is based on five years of data collected over seven years at a PCB-contaminated river that underwent remediation (dredging and monitored natural recovery). We considered PCB concentrations in sediment, water, and aquatic macroinvertebrates as potential predictors of PCB concentrations in tetragnathid spiders. Our specific objectives were to determine: 1) if PCB concentrations in our potential predictors (sediment, water, and aquatic macroinvertebrates) correlated with tetragnathid spider PCB concentrations; and 2) if those relationships were consistent across years. Note, the goal of the present study was not to determine the impact of dredging, but rather to use the environmental disruption caused by dredging to examine the relationship of contaminants in tetragnathid spiders to those in other aquatic endpoints surrounding an extreme environmental perturbation.

## 2. Material and methods

### 2.1. Sampling stations

In 2008, U.S. EPA Office of Research and Development and the U.S. EPA Great Lakes National Program Office conducted an extensive evaluation of the remedial project at the lower Ottawa River. The primary contaminant of concern for the remediation was PCBs occurring at high concentrations in sediment, and secondarily, polycyclic aromatic hydrocarbons (PAHs), lead, and oil/grease (Wescott, 2011). The lower Ottawa River is the lower 8.8 km of the river near its terminus in Lake Erie in southeast Michigan and northwestern Ohio (USA) and is a part of the Maumee River Area of Concern (AOC) (Fig. S1). During 2010, targeted hydraulic dredging was used for the sediment removal and disposal of ~183,500 $m^3$ of sediment at 31 noncontiguous locations in the lower Ottawa River (Wescott, 2011). For more information on the lower Ottawa River see Mills et al. (2017).

PCB concentrations were measured in 2009 before dredging and after dredging in 2011, 2012, 2013, and 2015. Media collected for analysis included sediment, water, macroinvertebrates, and tetragnathid spiders at 18 stations (10 from dredged locations and 8 from non-dredged locations) (Tables S1 & S2).

### 2.2. Sediment & water sampling

Mid-depth water column samples were collected using a Van Dorn, Niskin or similar type sampler after completing a triple rinse in the field with care not to disrupt the sediment before sample collection. After water sampling was completed, a composite sediment sample was collected from the top 15 cm of sediment. At each station 16 surface sediment core samples (top 15 cm) were collected around the boat for multiple analyses. If the sediment surface within a core sample appeared disturbed (e.g., debris interference, slumping, gaps in the sediment core), then the sample was discarded, and a new one was collected. After all cores were collected at a station, they were composited using a mechanical mixer with stainless-steel paddle or Kynar®-coated utensils to achieve a homogeneous sample of uniform color and consistency, then transferred into certified-clean sample containers. After collection was complete, all water and sediment samples were immediately placed on ice in the dark for transport to the laboratory where they were held at 4 °C until analyses. Samples were collected between July and August each year at each station.

### 2.3. Aquatic macroinvertebrate sampling

Artificial substrate samplers (Hester Dendys, HDs), modified from Hester and Dendy (1962), were used to collect aquatic macroinvertebrates. Individual HDs were constructed using either nine (2009, 2011, 2012, 2013) or 11-tempered pieces (2015) of pressed wood plates spaced with nylon washers and an eyebolt. The nine-plate design used 7.6 cm × 7.6 cm plates and the 11-plate design used 12.7 × 12.7 cm plates. Duplicate sets of HDs were deployed at each station each year to collect biomass for chemical analysis. Sets of HDs were deployed at shallower sites 25 cm above the sediment and at deeper sites 45 cm above the sediment. Sets of HDs were retrieved after ~42 days by raising the deployments with minimal disturbance to avoid losing macroinvertebrates. Sets of HDs from a station were placed in a clean plastic bag and covered with water from their respective station. To collect the macroinvertebrates, the samplers were deconstructed into the site water

and sieved (425 μm mesh). All organisms were sorted in the field using forceps to separate the macroinvertebrates and were composited into glass jars. Jars were frozen and stored at −20 °C until analyses. Macroinvertebrates were collected between August and October each year at each sampling station.

Additional HDs were deployed at six stations (three each from dredged and not dredged stations during each sampling year (except 2015) during the same time periods. These samples were collected to assess community condition (e.g., density estimates), using the taxonomically identified macroinvertebrates (following OEPA, 2015) being utilized for chemical analysis. Additionally, biomass (ash-free dry mass) was calculated using taxon-specific allometric equations (Benke et al., 1999).

### 2.4. Spider sampling

Riparian spiders (family Tetragnathidae) were collected from their webs by gloved hand at night within 1 m of the shoreline at each sampling station. Generally, 200 m of shoreline was sampled at each station, 50 m segments upstream and downstream, on both banks from a central cross-channel transect. One to four replicate samples of spiders (each containing 16 to 40 individuals) were collected at each station each year, based on abundance. Spiders were stored in glass jars on ice in the field and frozen in the laboratory at −20 °C until analyses. Samples were collected between August and early October each year.

### 2.5. PCB analysis

#### 2.5.1. Instrumentation analysis

One-liter samples of water were fortified with surrogate internal standards (SIS) and extracted three times with methylene chloride using a separatory funnel and combined. Approximately 20 g of wet sediment was mixed with sodium sulfate, fortified with SIS, and extracted with methylene chloride three times using a shaker table and combined. All extracts were dried over anhydrous sodium sulfate and cleaned using alumina columns, activated copper, and size exclusion high-performance liquid chromatography (HPLC).

Macroinvertebrate and spider tissues were homogenized prior to extraction using stainless-steel or titanium implements. Each homogenized sample was aliquoted for extraction into a Teflon® bottle and extracted three times with methylene chloride and sodium sulfate using Tissuemizer® (Tekmar, Cincinnati, OH, USA) techniques. The combined extract was dried over anhydrous sodium sulfate and cleaned using an alumina column and HPLC.

The post-HPLC extract for all samples was solvent exchanged to *n*-hexane, concentrated to either 0.5 mL or 1 mL and fortified with a set of internal standards (ISs). All extracts were analyzed for 121 PCB congeners (Table S3) via GC/MS in the SIM mode based on U.S. EPA Method 1668A (U.S. EPA, 1999) and quantified using the method of internal standards. Sediment, water, and biota samples were reported as μg/kg dry weight, ng/L, and ng/g wet weight, respectively. Total PCB concentrations were calculated by summing the 121 PCB congeners.

#### 2.5.2. Quality assurance/quality control

The average method detection limit (MDL) was 0.04 ± 0.02 (standard deviation, SD) ng/g and 0.11 ± 0.05 (SD) ng/L for all congeners in all sediment/biota and water samples, respectively. All sample results below the MDL were assigned a value of 0. If all congeners for an individual sample were below their respective MDL, the sample was removed from the analysis. A laboratory control sample, duplicate matrix spiked samples (PCB 34 & PCB 152), and duplicate method blanks were run at least once per batch of 20 samples and were extracted and analyzed identically to field samples and laboratory control. Method blanks were always below the detection limit. Mean recovery of laboratory control samples was 83.9 % ± 10.0 (SD) among all samples. The average recovery for all matrix spiked samples was 96.1 % ± 34.4 (SD), and the relative percent difference between matrix spiked samples and their duplicates was 6.37 % ± 6.1 (SD).

### 2.6. Lipid analysis

Percent lipids (as total extractable organics) in macroinvertebrate and spider tissue samples were determined gravimetrically for the purpose of normalizing PCB samples across time and stations. Briefly, an aliquot of pre-alumina sample from the solvent extraction was dried at 40 °C for approximately 5 min. The percent lipids were determined by gravimetric analysis of the extract residue after the solvent evaporated. All results were reported as percent lipids on a wet weight basis. Lipid normalization was calculated using the formula: Total PCB concentration/ (% lipid/100).

### 2.7. TOC analysis

Total organic carbon (TOC) analysis was performed on all sediment and water samples following procedures based on ASTM D4129-82 (U.S. EPA, 2004) and modified for soil and sediment matrices for the purpose of normalizing PCB samples across time and stations. Sample preparation consisted of drying, homogenizing, and acidifying to remove carbonates and bicarbonates. The samples were combusted in a high-temperature furnace in a stream of oxygen to form carbon dioxide ($CO_2$), which was analyzed using a $CO_2$ coulometer. Interfering gases, such as halogens, sulfur, nitrogen oxides, and water, were removed by chemical scrubbers prior to $CO_2$ measurement. Sediment and water results were reported in percent carbon on a dry weight basis, and all water and sediment samples were TOC-normalized using the formula: Total PCB concentration/ (% TOC/100).

### 2.8. Data analysis

Due to biomass constraints, sample-specific percent lipid content was not available for each macroinvertebrate and spider sample from all stations in all years. For macroinvertebrates, sample-specific lipid concentrations were used when possible (~96 % of samples) and the overall mean (across all years and sites) lipid concentration was used for samples missing lipid concentrations. All spider PCB concentrations were normalized to the seven-year station-specific mean lipid concentration.

Prior to analysis, all contaminant concentrations were $\log_{10}$ transformed to meet model assumptions.

To test year-to-year differences, spider PCB concentrations were modeled using sediment, water, and macroinvertebrate PCB concentrations separately using 2-way analysis of covariance (ANCOVA) models with year as a fixed effect. The relationship between covariates and spider PCB concentration was allowed to vary between years by including a full-factor model with a year-by-covariate interaction to test the assumption that covariates did not interact with spider concentrations differently among years. In the event of a non-significant interaction (all cases, $p > 0.05$), the interaction term was removed, considering year as a fixed block effect. All models included year first, and analyses were based on type I SS. All models were assessed for normality (Shapiro-Wilks test on residuals, $p > 0.01$) and assumptions of linearity and heteroskedasticity were visually assessed. Studentized residuals were ensured to be <3 in all but two data points. These data points were ensured to have little influence on the estimated slopes (Cook's D ≪ 1).

To test the relationship between each of the potential predictors (sediment, water, and macroinvertebrates), we calculated Pearson's correlation coefficients and tested whether the correlation was different than zero (2-tailed *t*-test, $\alpha = 0.05$).

To test the individual influence of each predictor on spider PCB concentrations, we utilized a multivariate regression analysis. Year was included as a fixed effect, with sediment, water, and macroinvertebrate PCB concentrations as covariates, in that order. Models were assessed for normality (Shapiro-Wilks test on residuals, $p > 0.01$) and assumptions of

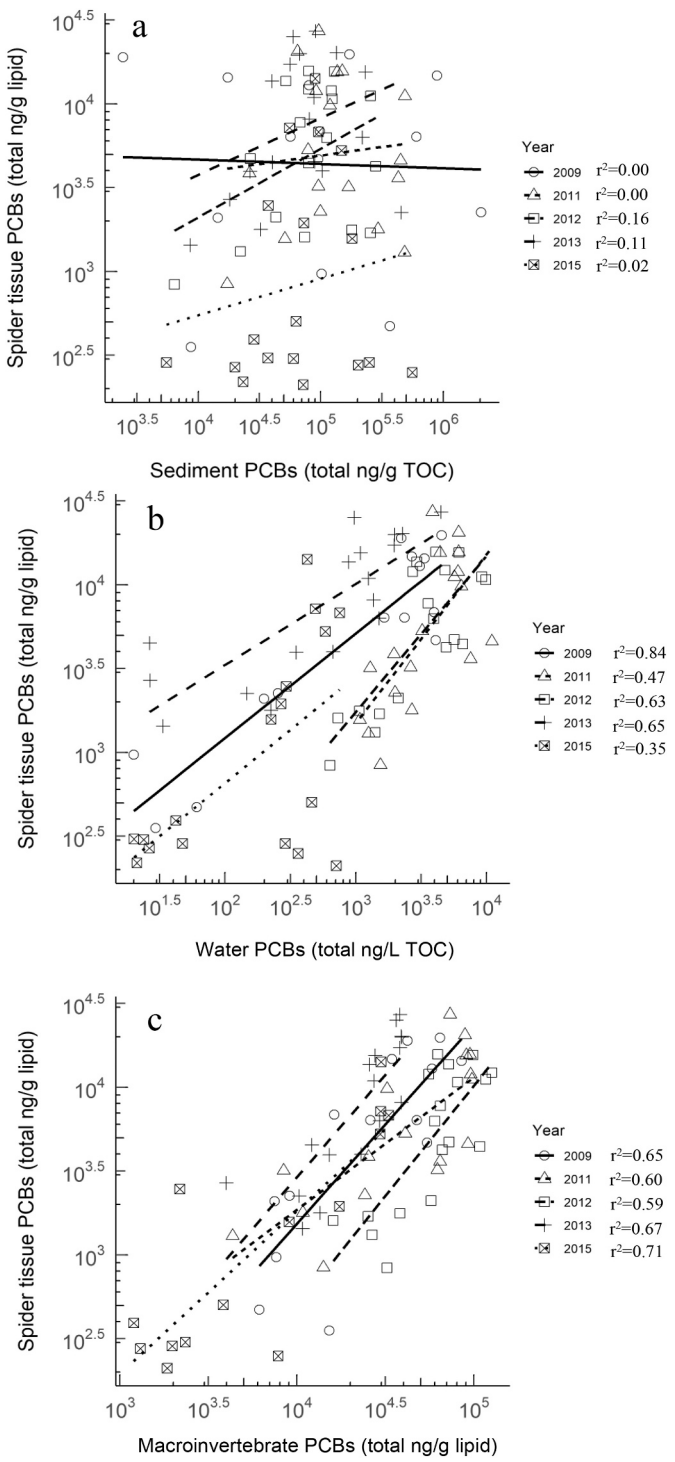


**Fig. 1.** Annual comparisons of total PCB concentrations in spiders (ng × $g^{-1}$ × $lipid^{-1}$) compared to a) sediment (ng × $g^{-1}$ × $TOC^{-1}$), b) water (ng × $L^{-1}$ × $TOC^{-1}$) and c) macroinvertebrates (ng × $g^{-1}$ × $lipid^{-1}$). Lines represent results of 2-way ANCOVA and show year-specific relationships (r2) of spiders with sediment, water, and macroinvertebrates. *TOC = total organic carbon.*

linearity and heteroskedasticity were visually assessed. Studentized residuals were ensured to be <3 and Cook's D < 1 for all data points. Variance inflation factor (VIF) was ensured to be <5 for all covariates. VIFs were calculated using the *vif()* function in the *car package*. Model predictions were output and visualized using the *ggplot2* package (Wickham et al., 2016).

All analyses were conducted in R version 4.0.3.

## 3. Results

### 3.1. Spider relationships to sediment, water, and macroinvertebrates

#### 3.1.1. Spiders v sediment

Spider PCB concentrations did not correspond to sediment PCB concentrations (Fig. 1a). There was not a significant interaction between year and sediment PCB concentration ($F_{4,76} = 0.581$, $p = 0.677$), so the term was removed. The final model, with year as a fixed effect and sediment PCB concentration as a covariate, was significant ($F_{5,80} = 8.17$, $p < 0.0001$, $r^2 = 0.34$). There was a significant effect of year ($F_{4,80} = 9.77$, $p < 0.0001$), but sediment PCB concentration was not a significant predictor of spider PCB concentration ($F_{1,80} = 1.78$, $p = 0.186$). Post-hoc pairwise comparisons indicated that spider PCB concentration was lower in 2015 relative to 2009, 2011, 2012, and 2013 (Tukey's HSD, $p < 0.05$); spider PCB concentrations were similar to one another in all other years.

#### 3.1.2. Spiders v water

Spider PCB concentrations were strongly and positively correlated to water PCB concentrations (Fig. 1b). There was not a significant interaction between year and water PCB concentration ($F_{4,74} = 1.241$, $p = 0.301$), so the term was removed. The final model, with year as a fixed effect and water PCB concentration as a covariate, was significant ($F_{5,78} = 32.48$, $p < 0.0001$, $r^2 = 0.68$). There was a significant effect of year ($F_{4,78} = 18.23$, $p < 0.0001$). After accounting for year, for which spider PCB concentrations were lower in 2015 relative to 2009, 2011, 2012, and 2013 (Tukey's HSD, $p < 0.05$), water PCB concentration was a highly significant predictor of spider PCB concentrations ($F_{1,78} = 89.47$, $p < 0.0001$). The lack of a significant year × water interaction indicated that the correlations between water PCB concentration and spider PCB concentrations were consistent among years ($\beta = 0.63$).

#### 3.1.3. Spiders v macroinvertebrates

Spider PCB concentrations were strongly and positively correlated to macroinvertebrates PCB concentrations (Fig. 1c). There was not a significant interaction between year and macroinvertebrate PCB concentration ($F_{4,70} = 0.974$, $p = 0.427$), so the term was removed. The final model, with year as a fixed effect and macroinvertebrate PCB concentration as a covariate, was significant ($F_{5,74} = 37.6$, $p < 0.0001$, $r^2 = 0.72$). There was a significant effect of year ($F_{4,74} = 15.35$, $p < 0.0001$), and macroinvertebrate PCB concentration was a highly significant predictor of spider PCB concentration ($F_{1,74} = 126.62$, $p < 0.0001$). Post-hoc pairwise comparisons indicated that, when controlling for macroinvertebrate PCB concentration, spider PCB concentrations were lower in 2015 relative to 2009, 2011, 2012, and 2013 (Tukey's HSD, $p < 0.05$); spider PCB concentrations were similar to one another in all other years.

Macroinvertebrate PCB concentration corresponded to spider PCB concentration similarly among years with a 1:1 relationship overall ($\beta = 1.023$). The lack of a significant year × macroinvertebrate interaction indicated that this correlation was consistent between years. Across all the years, chironomids accounted for between 72 and 92 % of the biomass collected from the HD deployments depending on the year (Table S4).

### 3.2. Overall relationships between sediment, water, and macroinvertebrates

Sediment PCB concentration was weakly but significantly and positively correlated with water PCB concentration ($\rho = 0.34$, $p < 0.01$; Fig. 2), but sediment PCB concentration was not correlated with macroinvertebrate PCB concentration ($\rho = 0.05$, $p > 0.05$). Water PCB concentration was strongly and positively correlated with macroinvertebrate PCB concentration ($\rho = 0.79$, $p < 0.001$).

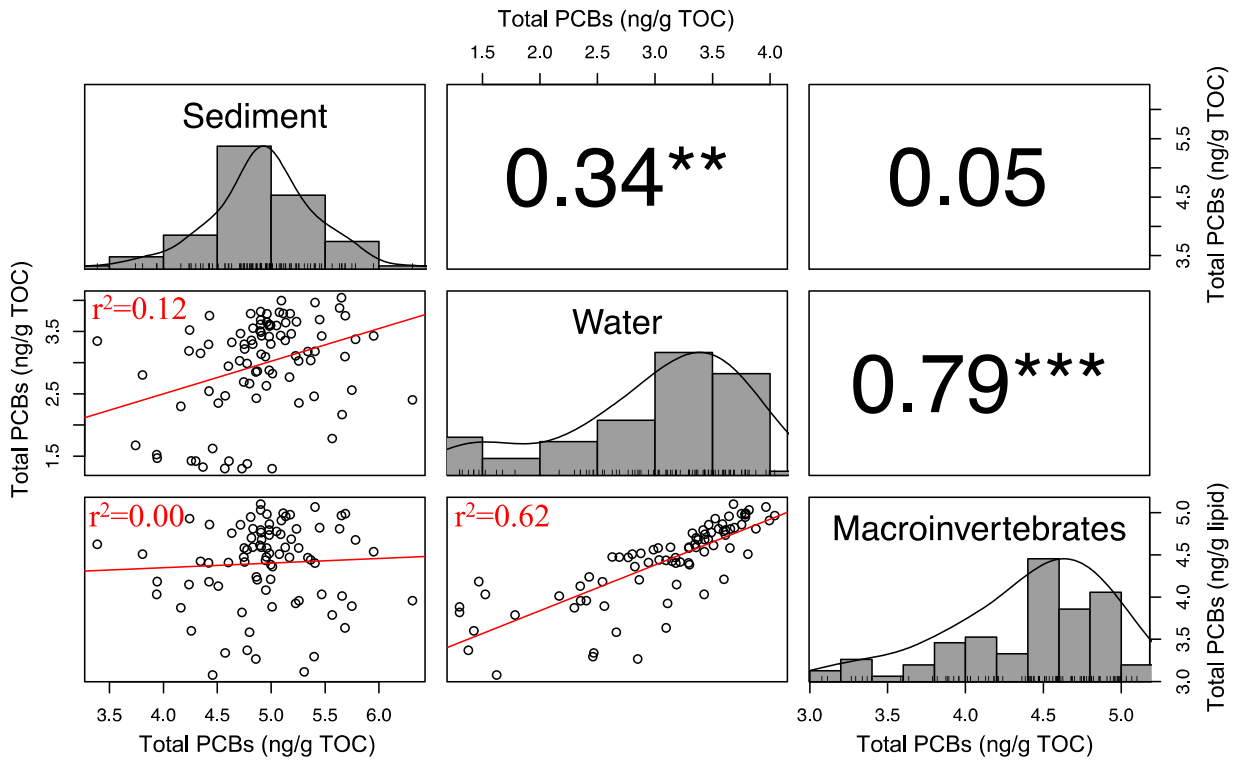


**Fig. 2.** Total PCB comparisons between potential predictor variables (sediment, water, macroinvertebrates). Whole study sample distributions of sediment (ng × $g^{-1}$ × $TOC^{-1}$), water (ng × $L^{-1}$ × $TOC^{-1}$) and macroinvertebrate total PCB concentration (ng × $g^{-1}$ × $lipid^{-1}$) are on the diagonal. Below the diagonal, data points are plotted with simple linear regression functions (red line). Pearson correlation coefficients (ρ) and significance (** = $p < 0.01$, *** = $p < 0.001$) are denoted in the respective squares above the diagonal. *TOC = total organic carbon.*

### *3.3. Individual influence of sediment, water, and macroinvertebrates on spider PCB concentrations*

The result of our multiple regression analysis indicated that sediment PCB concentrations remained a poor predictor of spider PCB concentrations, even after accounting for water and macroinvertebrate PCB concentrations ($F_{1,70} = 1.58$, $p = 0.213$). Water PCB concentration had a highly significant, positive relationship with spider PCB concentration ($F_{1,66} = 112.68$, $p < 0.0001$; $\beta = 0.316$). After accounting for the effect of water on spider PCB concentrations, macroinvertebrate PCB concentration continued to be significantly and positively related to spider PCBs ($F_{1,70} = 33.143$, $p < 0.0001$, $\beta = 0.720$), regardless of the significant correlation between water and macroinvertebrate PCB concentrations ($\rho = 0.79$). These results indicated that both macroinvertebrate and water PCB concentrations strongly correlate and have an additive effect on spider PCB concentration, with each covariate adding significant predictive power to spider PCB concentration. The overall model (all years and predictor variables considered individually) and their specific parameters are available in Eq. (S1).

## 4. Discussion

Riparian spiders from the family Tetragnathidae have been used by previous researchers as sentinels of aquatic pollution for various contaminants including metals (Otter et al., 2013), mercury (Tweedy et al., 2013; Speir et al., 2014), and PCBs (Walters et al., 2008; Walters et al., 2010; Kraus et al., 2017; Walters et al., 2018). Our study goal was to use a spatially and temporally extensive dataset to investigate if PCB concentrations in tetragnathid spiders were consistently correlated to PCB concentrations in surface sediment, water, and aquatic macroinvertebrates. Unique elements of this particular data set compared to prior studies using spiders as sentinels of aquatic pollution were that 1) it spanned five field seasons over a seven year sampling window rather than a single year or season; 2) pre- and post-remediation sampling bracketed a major environmental disturbance via remedial dredging; and 3) it included a relatively large number of sites (18 stations) spanning a large gradient of PCB concentrations (e.g., roughly 3 orders of magnitude across environmental samples) in the same river.

Concentrations of PCBs in sediment did not show a significant correlation to spider concentrations (Fig. 1a). Results from the present study differ from previous studies where bulk sediment concentrations were found to reflect PCB concentrations in biota. For example, Walters et al. (2010) showed a significant positive correlation between sediment PCBs and three different web-building taxa of spiders (including tetragnathids, $r^2 = 0.79$) during a single collection in 2007. Kraus et al. (2017) had similar results to Walters et al. (2010) when they combined two web-building riparian spider taxa (including tetragnathids) over three years and found a significant relationship between sediment and combined spider PCB concentrations ($r^2 = 0.41$).

The present study is the first to show a significant relationship between tetragnathid PCB concentrations and water samples. PCB concentrations in spiders were significantly correlated with water PCB concentrations during each year (Fig. 1b), despite a significant effect of year. These results support the work of previous researchers that have shown tetragnathid spiders to be connected to the aquatic environment (Baxter et al., 2005; Walters et al., 2008; Speir et al., 2014). For example, Walters et al. (2008) showed that tetragnathid spiders were part of an aquatic food web at a PCB contaminated site in South Carolina (USA) using carbon and nitrogen stable isotope signatures from a variety of taxa. Speir et al. (2014) plotted the trophic positions of aquatic and terrestrial organisms versus methyl-mercury concentrations and found that tetragnathid spiders were more closely aligned with the aquatic food web rather than the terrestrial food web associated with small ponds.

Spider PCBs were also significantly correlated with macroinvertebrates PCBs (Fig. 1c) despite year-to-year differences in

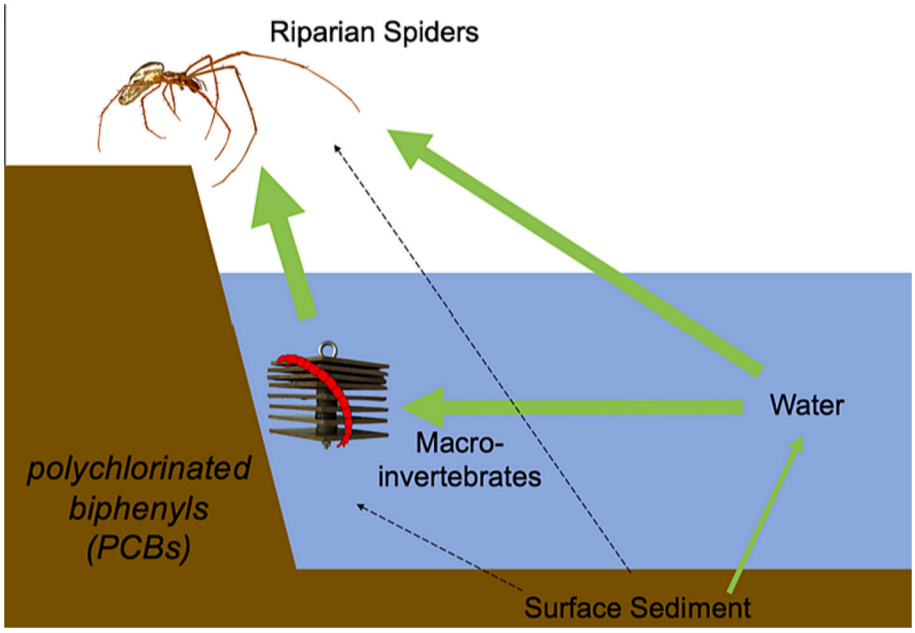


**Fig. 3.** Relationship model of overall study results. Green arrows represent significant relationships between matrices, with wider arrows representing stronger correlations. Dashed black lines represent relationships that were tested but were not significant.

concentrations. Tweedy et al. (2013) also observed a relationship between spiders and aquatic insects when they used experimental ponds to investigate the relationship between methylmercury in tetragnathid spiders and adult aquatic insects (chironomids and micro caddisflies) over six weeks. Like Tweedy et al. (2013), chironomids (midges), were the dominant aquatic insect taxa collected in the Ottawa River. However, in this study, larval aquatic insects (pre-metamorphosis) were used for the analysis rather than adult aquatic insects.

We investigated the relationships among predictor variables (sediment, water, macroinvertebrates) pooled across years. Water PCB concentrations were significantly correlated with PCB concentrations in macroinvertebrates (strong correlation) and sediment (weak correlation), yet no relationship existed between sediment and macroinvertebrates (Fig. 2). The lack of connection between sediment and biota (both spiders and macroinvertebrates) was surprising and highlighted the complex dynamics between bulk sediment concentrations and contaminant bioavailability at a given site (Verweij et al., 2004; Mackenbach et al., 2014).

We observed a study-wide 1:1 ratio between PCB concentrations in spiders and macroinvertebrates. In other words, for each 1-unit increase in macroinvertebrate PCB concentration, we observed a 1-unit increase in spider PCB concentrations. These results were unexpected because PCBs biomagnify in food webs; therefore, we expected to see higher concentrations in predators (spiders) than prey (macroinvertebrates). Our multivariate analysis results showed that spider PCB concentrations were significantly correlated with water concentrations, after removing the variability explained by macroinvertebrates. If we assume that these spiders were not ingesting a significant amount of PCBs directly from the water, our 1:1 ratio result indicates that these spiders may have been eating other prey items linked to the water, but not captured using our HD deployment. Another plausible explanation for the 1:1 ratio observed between PCB concentrations in spiders and macroinvertebrates involves contaminant shedding during insect metamorphosis. Kraus et al. (2014) published a meta-analysis investigating the effect of insect metamorphosis on contaminant body burden and showed that metamorphosis can have congener-specific effects on the concentration of PCBs retained in adult insects. If certain PCB congeners were not fully retained in the emergent insects as they transformed into adult insects, then aquatic macroinvertebrates PCB concentrations would not perfectly reflect concentrations in adult insects (post-emergence), which are the actual food item for riparian spiders. The 1:1 ratio results of the present study are similar to those from another PCB dredging area in 2011 (Ashtabula, Ohio, USA) where no obvious differences between tetragnathid spiders and larval aquatic macroinvertebrates PCB concentrations were observed at four co-located sampling locations (Meier et al., 2015; Walters et al., 2018). Interestingly, when Walters et al. (2010) collected adult aquatic insects (post metamorphosis) and spiders along a gradient of PCB contaminated sediment, they showed that when PCB sediment concentrations were highest, spider PCB concentrations were higher than those found in adult aquatic insects, but as sediment concentrations decreased, adult aquatic insects had higher PCB concentrations than spiders from the same system. Congener-specific PCB analysis was outside the scope of the present study, but our results highlight the need for research into the influence of insect metamorphosis on insect-mediated PCB flux.

## 5. Conclusions

This study investigated PCB concentrations in tetragnathid spiders and potential predictors (sediment, water, aquatic macroinvertebrates) utilizing 18 sampling stations over a seven-year period that spanned a major dredging event. To best summarize our findings, we developed a relationship model of our results highlighting the strength of each relationship (Fig. 3). Our results showed that spiders PCB concentrations consistently correlated with year-to-year fluctuations in PCB concentrations in aquatic macroinvertebrates and water, but never with sediment.

Overall, the results of the present study fill a critical knowledge gap for the utilization of tetragnathid spiders as sentinels of aquatic pollution by showing that despite year-to-year changes in PCB concentrations, consistent relationships existed between spiders and other biotic (aquatic macroinvertebrate) and abiotic (water and sediment) endpoints.

## Disclaimer

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

## CRediT authorship contribution statement

**Ryan R. Otter:** Data curation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Marc A. Mills:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Ken M. Fritz:** Conceptualization, Data curation, Investigation, Writing – review & editing. **James M. Lazorchak:** Conceptualization, Investigation, Methodology, Resources, Writing – review & editing. **Dalon P. White:** Formal analysis, Software, Visualization, Writing – review & editing. **Gale B. Beaubien:** Writing – original draft, Writing – review & editing. **David M. Walters:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data pertaining to this manuscript are deposited from the U.S. Geological Survey ScienceBase: USGS Data Release (IP-159137).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.169230.

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