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Differential Accumulation of Polychlorinated Biphenyl Congeners in the Terrestrial Food Web of the Kalamazoo River Superfund Site, Michigan

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A series of field studies was conducted to determine the bioaccumulation of polychlorinated biphenyl (PCB) congeners in the terrestrial food web of the Kalamazoo River flood plain. Samples included colocated soils, native plants likely to be consumed by wildlife, several taxa of terrestrial invertebrates, small mammals, passerine bird eggs, nestlings, and adults, and great horned owl plasma and eggs. Mean concentrations of total PCBs in samples from the former Trowbridge impoundment were 6.5 mg/kg dry weight for soils and 0.023, 0.13, 1.3, 1.3, 1.6, and 8.2 mg/kg wet weight for plants, small herbivorous mammals, depurated earthworms, shrews, great horned owl eggs, and house wren eggs, respectively. Historical data from the Kalamazoo River have reported Aroclor-equivalent total PCB concentrations in the terrestrial food web; however, the degree of environmental weathering of the parent PCB mixtures was unknown. In this study, earthworms and composite samples of coleoptera exhibited PCB congener patterns that were similar to patterns in colocated soils. However, in plants, less chlorinated PCBs (e.g., mono-, di-, tri-, and tetrachlorinated biphenyls) were predominant, and in small mammals, there was a notable enrichment of PCBs 153, 180, 138, 118, and 99. In general, concentrations of PCBs were lower in most biota than in soil from the Kalamazoo River Area of Concern (KRAOC) although there was a modest biomagnification of PCBs from lower trophic level biota to higher trophic levels. As a consequence of environmental weathering of PCBs in the terrestrial food web of the KRAOC, the relative potency of the PCBs (expressed as mg TEQs/kg PCBs) decreased from soil to most biota. While there was a general trend, as expected, in which concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) increased with total PCBs, this relationship was rather poor ($R^2 = 0.13$). Taken together, these data suggest that the differential accumulation of PCB congeners in the terrestrial food web can be explained by congener-specific differences in bioavailability from soil, exposure pathways, and metabolic potential of each of the food web components.

Introduction

In 1990, approximately 80 miles of the Kalamazoo River was designated a Superfund site, referred to as the Kalamazoo River Area of Concern (KRAOC). The site extends from Morrow Dam in Kalamazoo County to Lake Michigan (Figure 1). The release of polychlorinated biphenyls (PCBs), the primary contaminants of potential ecological concern (COPECs), resulted from PCB-contaminated waste discharged from the recycling and processing of carbonless copy paper (*1*). During the period from 1957 to 1971, the ink solvent used in carbonless copy paper contained mixtures of PCBs, primarily Aroclor 1242 (*2*). Aroclor 1254 may also have been added to inks and other additives in lesser amounts (*2*). The majority of PCBs in the Kalamazoo River watershed are associated with sediment deposits in a series of impoundments. However, partial removal of three dams (e.g., Plainwell, Otsego, and Trowbridge) to their sill levels in the 1970s allowed substantial amounts of sediments to be transported downstream, lowered the water levels to the sill of the dams' spillways, and exposed former sediments in the former impoundments. Much of the exposed former sediment is within the flood plain and thus becomes periodically inundated during high flow events.

PCBs are an environmentally ubiquitous, complex mixture of individual compounds that are chlorinated with 1−10 chlorines in various combinations of positions to create a total of 209 possible congeners. Historically, site-specific PCB data from samples collected from the KRAOC have been quantified as Aroclors 1016, 1242, 1248, 1254, and/or 1260 (*1*). However, the analytical methodologies used in these investigations (i.e., EPA Methods 8080 and 8081) do not measure "Aroclors" but rather a pattern of PCB congeners. The analyst then determines the Aroclor pattern that most closely approximates that mixture of PCB congeners. In some cases, the PCBs were quantified as a particular Aroclor simply because that Aroclor or mixture of Aroclors was used as the standard.

Each Aroclor is a complex mixture of numerous PCB congeners, and each congener behaves independently once released to the environment. Due to selective volatilization, degradation, accumulation, sorption, and metabolism (i.e., collectively termed "environmental weathering"), the relative concentrations of congeners in a mixture or matrix change as a function of time. Limitations associated with Aroclor-based determination of PCBs in environmental samples have been recognized for a long time (*3*−*6*) and have been acknowledged by the U.S. EPA (*7*, *8*) and the National

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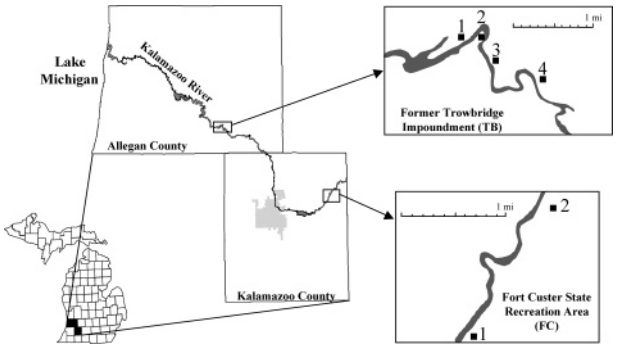

FIGURE 1. Site location map for the sampling grids at the former Trowbridge impoundment (TB) and the Fort Custer (FC) reference area along the Kalamazoo River, Michigan.

Research Council (*9*). In addition, there are difficulties and uncertainties with assessing the toxicity of environmentally weathered PCB mixtures that are quantified as Aroclors. Congener-specific analysis, including coplanar PCB congeners combined with a calculation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents (TEQs), is generally thought to correlate better with toxicity than measures of total PCBs (*10*−*12*). However, recent work by Custer et al. (*13*) calls into question whether toxic equivalency factors (TEFs) developed for PCBs are appropriate to predict effects in some bird species.

While considerable work has been conducted on the environmental fate and bioaccumulation of PCB congeners in aquatic habitats (*14*−*16*), very little is known about the environmental fate and bioaccumulation of PCB congeners in terrestrial systems. Therefore, the specific focus of the current study is the riparian, seasonally terrestrial/flood plain habitat along the Kalamazoo River. These flood plains are generally broad and covered with lowland forest or located within marshy wetlands. Specifically, wetland habitats within the Kalamazoo River watershed include marsh, wet meadow, wooded swamp, and bottomland forest. Associated water regimes range from permanently flooded for some marsh habitats to temporarily or seasonally flooded for the wet meadow and bottomland forest habitats. Wooded vegetation along the Kalamazoo River and flood plain consists of varying mixtures of willow, cottonwood, silver maple, and ash, with sycamores scattered throughout the lowland areas. Extensive wetlands along the river contain varying amounts of purple loosestrife, cattails, sedges, rushes, and aquatic species such as pond weeds and water lilies. In the former impoundments, there are large open areas dominated by *Ambiosia trifida* (giant ragweed), *Urtica dioica* (stinging nettles), *Elytrugia repens* (quack grass), *Conium maculatum* (poison hemlock), *Alliarria petiolata* (garlic mustard), and *Silica alba* (white campion). Riparian habitats along the Kalamazoo River provide food and forage for diverse species of wildlife.

These areas of intermittently flooded wetland soils have substantially different ecological functions compared to true sediments in permanently flooded areas and also have substantial differences in chemical fate, transport, bioavailability, and wildlife exposure. Delineation between soil and sediment within wetland habitats becomes arguably more difficult in such areas and based on traditional criteria may or may not coincide with a delineation that is most appropriate for the management of risk for receptors of concern. One approach for delineation can be based on the habitat it supports and other factors such as duration of water inundation, exposure potentials for key receptors, bioavailability, concentrations of PCBs, concentrations of organic matter, vegetation types, and prevalence of invertebrate type (benthic or terrestrial). Taken together, site-specific wildlife exposure data and site-specific conceptual site models support the conclusion that key receptor exposures likely diverge at the invertebrate level within wetland habitats under the premise that terrestrial invertebrates are associated with soils and benthic invertebrates are associated with sediments.

The focus of the current investigation was the intermittently flooded wetland soils and the accumulation of PCBs in the associated terrestrial food web. The purposes of this study were to (1) determine congener-specific PCB concentrations and relative patterns of congeners in terrestrial samples collected from the Kalamazoo River flood plain, (2) compare congener concentrations and patterns spatially and temporally between locations, (3) examine and contrast congener concentrations and patterns among trophic levels to gain a better understanding of the dynamics and accumulation of PCBs in a terrestrial food web, and (4) compare the relationship between concentrations of total PCBs and TEQs across multiple levels of the terrestrial food web. The results presented here are part of a larger and more comprehensive set of field investigations that were designed to gather site-specific data on the concentrations of individual PCB congeners. Taken together, the results from these studies will better define PCB exposures by determining site-specific dietary composition of key receptors, PCB concentrations in site-specific prey items, tissue residue levels in key receptors, and data necessary to develop a food web model that can be used to address movement of PCBs within the KRAOC food web.

Experimental Section

Study Area Locations. This study focused on two locations for food web analysis. Within the KRAOC, the former Trowbridge impoundment was selected as a study site since it is the largest of the three former impoundments (e.g., containing approximately 132 hectares of former sediments and 69 hectares of existing impounded water), has the greatest mass of PCBs, and has the greatest surficial mean concentration of PCBs in soils (approximately 11 mg/kg, dry weight (dw)) relative to the other former impoundments. Within the former Trowbridge impoundment (TB), four sampling grids were established within the flood plain (Figure 1). Fort Custer State Recreation Area (FC) was selected as a reference site for this study because it is upstream of the KRAOC and is relatively uncontaminated with PCBs. Specifically, FC is about 30 miles upstream of TB. Within the reference area at FC, two sampling grids were established within the flood plain (Figure 1).

Sampling Grid Design and Collection Methods. Most samples of plants, soils, above-ground invertebrates, subterranean invertebrates (earthworms), and small mammals were collected simultaneously (within a specified sampling period) within a 30 × 30 m^2 sampling grid. Specifically, plants, earthworms, and colocated soils were collected from a randomly selected 1 m^2 area within the sampling grid. A few samples were collected in close proximity but outside of specified sampling grids based on targeted species of plants and birds. For plant collections, at least 10 g of plant material was collected above the root crown. Also, seeds and/or fruits likely to be consumed by songbirds and those plant species previously identified as PCB bioaccumulators (Dave Charters, personal communication) were targeted. Soil samples were collected using a Wildco stainless steel core sampler (2 in. diameter; 20 in. length) or a bucket auger (2 in. diameter; 6 in. length). For earthworms, two composite samples of approximately 20 g were collected from each sampling grid during every sampling event. One earthworm composite sample (termed "nondepurated") was rinsed with water and analyzed for PCBs. The other earthworm composite sample ("depurated") was rinsed with water and allowed to depurate for 24−48 h.

All samples were collected under approved state and federal permits and in accordance with Michigan State University's All-University Committee on Animal Use and Care. Above-ground terrestrial invertebrates were collected by hand picking and sweep nets. Invertebrates were sorted and classified into orders before analysis. Small mammals, including the white-footed deer mouse (*Peromyscus leucopus*), red squirrel (*Tamiasciurus hudsonicus*), Eastern chipmunk (*Tamias striatus*), meadow jumping mouse (*Zapus hudsonicus*), meadow vole (*Microtus pennsylvanicus*), short-tailed shrew (*Blarina brevicauda*), and masked shrew (*Sorex cinereus*) were collected by setting 49 alternating Sherman live traps and pitfall traps that were placed within each sampling grid. Eggs and nestlings of house wren (*Troglodytes aedon*) and Eastern bluebird (*Sialia sialis*) were collected from nest boxes within the study areas. Adult house wrens and American robins (*Turdus migratorius*) were collected by either mist-netting or gunshot (*17*−*18*). Addled eggs and plasma from great horned owls (*Bubo virginianus*) were collected from natural nests or artificial nesting platforms within the TB and FC study areas.

Sampling Rounds. Samples were collected during the years of 2000, 2001, and 2002, with most samples being collected during 2000 and 2001. To address seasonal trends in concentrations of PCBs, samples were collected during distinct spans of time or "periods" during the spring and summer of 2000. Time periods for sample collections were as follows: period 1 for soils, plants, terrestrial invertebrates, and earthworms, May 22−June 21, 2000; period 2 for soils, plants, terrestrial invertebrates, and earthworms, July 17−Aug 16, 2000; period 3 for soils, plants, terrestrial invertebrates, and earthworms, Aug 24−Sept 19, 2000; period 1 for small mammals and shrews, June 7−July 20, 2000; period 2 for small mammals and shrews, Aug 26−Sept 19, 2000.

Analytical Methodology. Surrogate standards, PCB 204 (IUPAC) and PCB 30 (AccuStandard, New Haven, CT), were added to all samples, blanks, and matrix spikes before Soxhlet extraction. Each analytical batch consisted of 20 samples, at least one extraction blank, a matrix spike and matrix spike duplicate, laboratory spike, and standard reference material. PCBs including di- and mono-ortho-substituted congeners were quantified by use of a gas chromatograph (Perkin-Elmer AutoSystem) equipped with a J&W DB-5 30-m capillary column and a ^{63}Ni electron capture detector (GC-ECD). A solution containing 98 individual PCB congeners with known composition and content was used as a standard. Congeners were identified by comparing sample peak retention times to those of the known standard. In sample extracts, concentrations of each congener were determined by comparing the peak area to that of the appropriate peak in the standard mixture after an initial five-point calibration assured instrument linearity. PCB congeners were quantified by use of a gas chromatograph (Perkin-Elmer AutoSystem or Hewlett-Packard 5890 SII) equipped with a ^{63}Ni electron capture detector. Concentrations of all resolved PCB congeners were summed to obtain total PCB concentrations. The concentrations of the surrogate standards were calculated and used to determine extraction efficiency for each sample. A conservative estimate of the method detection limit for individual congeners is 1 ppt. This method detection limit is based on the injection volume of 1 μL, the signal-to-noise ratio of a 25 ppt standard, and the mass of sample extracted.

Non-ortho-substituted (coplanar) PCB congeners 77, 81, 126, and 169 were separated from coeluting congeners and interferences by cleanup on a carbon-impregnated silica gel column. Extracts were analyzed by GC-MS on a Hewlett-Packard 5890 series II gas chromatograph equipped with a Phenomenex ZB-5 30-m capillary column and a HP 5972 series mass-selective detector. Non-ortho-substituted PCB congeners were detected and confirmed by selected ion monitoring of the two largest ions of the molecular cluster. Congener concentrations were calculated based on ion ratios for the native and ^{13}C congener.

Calculation of TCDD Equivalents. Concentrations of TEQs in samples were calculated by multiplying the concentration of individual PCB congeners by its respective World Health Organization (WHO) toxic equivalency factor (TEF) (*19*). Total TEQ concentrations were determined by summing the concentrations of the TEQs of congener IUPAC numbers 77, 81, 105, 118, 126, 156, 157, 167, and 169. When a congener was not detected, a surrogate value of one-half of the limit of detection was multiplied by the TEF to calculate the congener-specific TEQ. The potential impact of assigning a proxy value of one-half the detection limit for the TEQ calculations was found to be minimal for samples from Trowbridge (data not shown). To test this, a ratio was calculated between the maximum estimated TEQ concentration (using the full detection limit for congeners that were not detected) and the minimum estimated TEQ concentration (using a value of zero for congeners that were not detected). As expected, with samples from Fort Custer, there was more uncertainty in the estimated TEQ concentrations as there were more congeners that were not detected. Due to the differing sensitivities of mammals, birds, and fish toward PCBs and other dioxin-like chemicals, three sets of TEF values have been developed for TEQ calculations that apply to mammalian, avian, and fish receptor species (*19*). When mono-ortho congeners coeluted with other PCB congeners, the total concentration for that coeluting pair was considered to be entirely due to the mono-ortho congener. Thus, for a sample with coeluting congeners, the TEQ concentration was overestimated.

Statistical Analysis. The Kolmogorov−Smirnov one-sample test with Lillifor's transformation was used to assess whether total PCB data sets were normally distributed. When data were normally distributed, analysis of variance (ANOVA) followed by Tukey's honestly significant difference (HSD) was used to detect significant differences among data sets (*20*). When data sets were not normally distributed, the nonparametric Kruskal−Wallis test was used to detect differences among data sets. When total PCBs between the TB and the FC locations were compared, the two-group t-test or the Mann−Whitney U-test was used if the data was normally distributed or nonnormally distributed, respectively. The criterion for significance that was used in all statistical tests was $p < 0.05$.

Results and Discussion

Ranges of PCB and TEQ Concentrations in Terrestrial Food Web Components. Concentrations of total PCBs and TEQs were significantly greater in terrestrial food web components from TB in the KRAOC than those from the upstream reference site at FC (Tables 1 and 2). Maximum observed concentrations were 36.3 mg/kg wet weight (ww) in a single house wren egg from TB and 0.47 mg/kg (ww) in a single great horned owl egg from FC. For avian TEQs, the maximum observed concentrations were 5500 ng/kg (dw) in soil at TB and 49 ng/kg (ww) in a shrew from FC. Average concentrations of total PCBs in soils from TB were approximately 700-fold greater than those of soils from the reference site. However, average concentrations of total PCBs in orthoptera (i.e., crickets and grasshoppers), plants, and small mammals (excluding shrews) from TB were only approximately 2-, 7-, and 6-fold greater than those of the reference area, respectively. Taken together, these data suggest that plants do not readily bioaccumulate PCBs from soil and that exposure to PCBs via soil and plant ingestion is likely minimal to herbivores relative to carnivores (discussed below). Some of the plants that were collected included those previously characterized as PCB bioaccumulator species such as grasses,

TABLE 1. Total PCB Concentrations (mg/kg, ww) in Soil and Soil-Associated Biota from the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site (FC)

	TB location				FC location			
	N	mean % lipid[a]	mean total PCBs (mg/kg)[b]	geometric mean (mg/kg)[b]	*N*	mean % lipid[a]	mean total PCBs (mg/kg)[b]	geometric mean (mg/kg)[b]
soil[a]	21	5.4	6.5 ± 4.7[e]	4.7	8	4.9	0.009 ± 0.009	0.005
plants	28	0.70	0.023 ± 0.044[e]	0.009	10	3.0	0.003 ± 0.003	0.002
terrestrial invertebrates[c]	30	5.6	0.34 ± 0.57[e]	0.10	18	4.2	0.023 ± 0.032	0.007
fresh earthworms	18	2.0	1.7 ± 1.8[e]	1.1	9	1.9	0.003 ± 0.001	0.002
depurated earthworms	14	2.2	1.3 ± 1.1[e]	0.86	7	1.8	0.006 ± 0.004	0.005
small mammals[d]	21	4.8	0.13 ± 0.16[e]	0.074	18	4.1	0.021 ± 0.042	0.007
shrews	17	2.9	1.3 ± 0.94[e]	0.85	16	4.2	0.009 ± 0.005	0.008
house wren eggs	21	10	8.2 ± 8.3[e]	5.8	15	13	0.12 ± 0.12	0.067
house wren nestlings	18	6.1	1.4 ± 2.7[e]	0.70	13	5.3	0.020 ± 0.020	0.015
house wren adults	9	5.4	3.2 ± 2.0[e]	2.6	8	4.6	0.072 ± 0.032	0.064
bluebird eggs	10	9.6	7.4 ± 5.3[e]	5.2	15	8.1	0.16 ± 0.10	0.13
bluebird nestlings	7	4.5	1.7 ± 2.33[e]	0.72	19	4.8	0.015 ± 0.013	0.012
American robin adults	17	4.3	0.92 ± 1.2[e]	0.30	4	2.3	0.091 ± 0.15	0.030
great horned owl plasma	7	0.49	0.045 ± 0.022	0.040	1	0.46	0.008	0.008
great horned owl eggs	4	7.2	1.6 ± 0.87	1.4	1	5.8	0.47	0.47

[a] Mean percent organic carbon reported for soils; mean ± standard deviation. [b] Concentrations of total PCBs (mg/kg, wet weight basis for biota and dry weight basis for soils) based on PCB congeners as described in text. [c] Earthworms were treated separately from other terrestrial invertebrates. [d] Shrews were treated separately from other small mammals. [e] Indicates a significant difference from the FC reference site at $p < 0.05$.

TABLE 2. Average Concentrations of Avian and Mammalian TEQs among Various Trophic Levels in the Terrestrial Food Web at Both the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site (FC)

	TB location					FC location				
		avian TEQs (ng/kg)[a]		mammalian TEQs (ng/kg)[a]			avian TEQs (ng/kg)[a]		mammalian TEQs (ng/kg)[a]	
	N	mean	geometric mean	mean	geometric mean	*N*	mean	geometric mean	mean	geometric mean
soil	21	1240 ± 1410[d]	303	77 ± 50[d]	55	8	0.79 ± 0.73	0.42	0.40 ± 0.49	0.24
terrestrial invertebrates[b]	30	80 ± 200[d]	12	7.5 ± 12[d]		18	1.6 ± 2.0	0.34	0.61 ± 0.74	
fresh earthworms	18	238 ± 255[d]	117	13 ± 8.1[d]	3.0	9	0.65 ± 0.48	0.54	0.41 ± 0.37	0.18
depurated earthworms	14	154 ± 186[d]	93	10 ± 9.5[d]	10	7	1.8 ± 4.0	0.47	1.1 ± 2.4	0.31
small mammals[c]	21	9.8 ± 19[d]	4.6	9.4 ± 20[d]	7.2	18	0.89 ± 1.0	0.58	0.70 ± 0.90	0.29
shrews	17	72 ± 69[d]	47	60 ± 56[d]	4.0	16	4.2 ± 12	1.3	3.7 ± 12	0.41
house wren eggs	21	423 ± 587[d]	250	*e*	*e*	15	6.0 ± 4.5	0.94	*e*	*e*
house wren nestlings	18	89 ± 117[d]	58	*e*	*e*	13	1.4 ± 0.96	1.2	*e*	*e*
house wren adults	9	107 ± 57[d]	91	*e*	*e*	8	7.1 ± 5.7	5.8	*e*	*e*
bluebird eggs	10	57 ± 60[d]	38	*e*	*e*	15	2.9 ± 4.7	1.3	*e*	*e*
bluebird nestlings	7	6.7 ± 4.7[d]	5.3	*e*	*e*	19	1.6 ± 1.3	1.3	*e*	*e*
American robin adults	17	3.9 ± 4.4	2.4	*e*	*e*	4	1.1 ± 0.55	0.96	*e*	*e*
great horned owl plasma	2	0.69 ± 0.79	1.6	*e*	*e*	1	*e*	*e*	*e*	*e*
great horned owl eggs	4	13 ± 10	11	*e*	*e*	1	8.4	8.4	*e*	*e*

[a] Concentrations of TEQs (ng/kg, wet weight basis for biota and dry weight basis for soils) based on PCB congeners as described in text; mean ± standard deviation. [b] Earthworms were treated separately from other terrestrial invertebrates. [c] Shrews were treated separately from other small mammals. [d] Indicates a significant difference from the FC reference site at $p < 0.05$. [e] Not calculated.

quackgrass, sumac, and aspen (Dave Charters, personal communication). However, in this study, there were no statistically significant differences in concentrations of total PCBs among these bioaccumulating species and any other plant samples that were analyzed.

Average concentrations of PCBs in coleoptera (i.e., beetles), house wren eggs, shrews, and depurated earthworms were approximately 50-, 70-, 150-, and 200-fold greater at Trowbridge than those from the reference area, respectively. The coleoptera samples included a considerable quantity of June bugs (*Phyllophaga* sp.) and Japanese beetles (*Popillia japonica*), the larval stage of which resides in soil as grubs. In addition, the larval stages of some coleopteran species are very rich in lipids (*21*), which combined with the contact with soil during this life stage may account for the greater accumulation of PCBs in coleopteran species as compared to that in orthopteran species, which are not as closely linked to the soil environment.

As no reports could be found in the literature comparing PCB uptake between fresh and depurated earthworms, concentrations of PCBs were compared in samples matched for the same sampling grid and time point. While variable and not statistically significant, the concentrations of PCBs at the TB sampling area tended to be greater in the fresh earthworms compared to those of depurated earthworms, whereas at Fort Custer concentrations of PCBs were all less in the fresh earthworms than the depurated earthworms (data not shown). At each sampling area, the relationship was found to be poor between concentrations of PCBs in soil (on a dry weight or organic-carbon-normalized basis) and fresh or depurated earthworms (on a wet weight or lipid-normalized basis; data not shown).

Due to its relatively great ingestion rate, relatively small home range (varies from 0.39 to 0.96 ha (*22*−*23*)), and its relatively short lifespan (approximately 1 year (*24*−*25*)), the short-tailed shrew has been recommended as a sentinel species of contaminant exposure based on trophic level and value as a bioindicator (*26*). At TB, shrews tended to have approximately 10-fold greater concentrations of total PCBs than other small mammals, such as white-footed mice, moles,

TABLE 3. Bioaccumulation Factors of Total PCBs (Organic-Carbon- and Lipid-Normalized) among the Terrestrial Food Web at the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site(FC)[a]

trophic transfer	TB location	FC location
Biota−Soil Accumulation Factor (BSAF)		
soil → terrestrial plant	0.016	2.5
soil → terrestrial invertebrates[b]	0.022	2.0
soil → earthworms (nondepurated)	0.66	0.99
soil → earthworms (depurated)	0.48	2.4
soil → small mammals	0.018	1.6
soil → shrews	0.35	1.6
soil → robin adults	0.080	10
soil → house wren eggs	0.76	6.1
soil → bluebird eggs	0.74	13
soil → great horned owl eggs	0.23	64
Biomagnification Factor (BMF)		
plant → small mammals	1.1	0.65
terrestrial invertebrates[b] → shrews	16	0.83
earthworms (depurated) → shrews	0.74	0.69
earthworms (depurated) → robin adults	0.17	4.4
terrestrial invertebrates[b] → house wren eggs	35	3.1
terrestrial invertebrates[b] → bluebird eggs	34	6.6
small mammals → great horned owl eggs	13	40

[a] Biomagnification calculations were made based on the assumption that total PCB concentrations in soils and biota and bioavailability of PCBs were homogeneous throughout each location. Animal data were normalized by lipid content, while soil data were normalized by organic carbon content. Calculations were based on geometric means. [b] Earthworms were treated separately from other terrestrial invertebrates.

and voles. This trend has been observed with other persistent, bioaccumulative compounds such as dichlorodiphenyltrichloroethane (DDT) (*27*). Thus, these data support the selection of the short-tailed shrew and similar species as ecological receptors of concern due to their relatively great potential for exposure relative to other terrestrial mammalian species.

When data for individual sampling grids within each location were compared, there were no statistically significant differences in concentrations of PCBs or TEQs among sampling grids within either the TB or the FC sampling areas (data not shown). In addition, there were no statistically significant temporal differences.

Bioavailability and Bioaccumulation. Except for eggs of house wrens and Eastern bluebirds, average concentrations of total PCBs in all food web items from TB were less than the average concentration of total PCBs in soil. When PCB concentrations were normalized to organic carbon for soils and lipids for biota, the accumulation of PCBs from soil (defined as the biota−soil accumulation factor or BSAF) was less than unity for all of the TB sample types (Table 3). Limited evidence suggests that bioavailability decreases over time as chemicals age in soil (*28*). This may be due in part to the relatively great binding affinity of many PCB congeners to particulate matter and the diffusion of PCB congeners into the soil lattice and Donnan spaces. Also, at TB, concentrations of total organic carbon in flood plain soils (with an average of approximately 5−6%) may further reduce bioavailability of PCBs. On the basis of available life history information, most of the target biota at TB would be expected to reside and forage within the contaminated flood plain. However, some of the species may not be year-round residents (e.g., passerine species). Thus, there is some uncertainty regarding what their exposures might be when these species are not at TB. The slightly greater concentrations of PCBs in passerine bird eggs compared to other sample types are likely due to a 13−15-fold biomagnification from terrestrial invertebrates (Table 3). Similar trophic-transfer biomagnification factors (BMFs) of approximately 8−10-fold were observed for insects to shrews and small mammals to great horned owls. While it should be noted that these are apparent BMFs since the actual diet is unknown, these data demonstrate the potential for biomagnification of PCBs in a terrestrial food web. Similar observations have been made for simple terrestrial food webs (*29*−*31*). The BSAF for earthworms at Trowbridge is similar to that observed for earthworms in the Rhine Delta flood plains, whereas the BSAF for shrews at Trowbridge is lower than those from the Rhine Delta flood plains (*31*).

However, in areas where PCB concentrations in soil are relatively low, such as with the FC reference area, PCB concentrations in some biota samples were greater than the concentrations in soil. In addition, the BSAFs for Fort Custer were greater than unity for several matrixes. In part, this may be due to a relatively greater influence of atmospheric input and other potential exposure pathways at the reference area. Alternatively, it may be possible that there are concentration-dependent differences in the efficiency of biota to uptake PCBs from soil. Taken together, these observations demonstrate that caution should be exercised when applying BSAFs across sites with greatly different PCB concentrations. Similar cautions have been raised in regards to the application of BSAFs from one site to another since there are potential differences in soil and sediment characteristics that may affect bioavailability (*32*).

PCB Congener Composition in Terrestrial Food Web Components. If differential environmental weathering of PCB congeners did not occur, then one might expect somewhat similar patterns of PCB congeners between soil and components of the terrestrial food web. However, there were clear qualitative differences (discussed in detail below) in the patterns of relative PCB congener concentrations in most components of the food web compared to that of soil (Figure 2). Exceptions to this generality included earthworms and coleoptera composite samples, which exhibited remarkably similar PCB congener patterns to colocated soils (Figure 2). As discussed earlier, the coleoptera samples included a considerable quantity of June bugs (*Phyllophaga* sp.) and Japanese beetles (*Popillia japonica*), the larval stage of which reside in soil as grubs. The intimate contact with soil for earthworms and the larval stages of the coleoptera samples coupled with their relative inability to metabolize PCBs are likely factors to explain the similar congener patterns that were observed.

For most of the other food web components, the PCB congener patterns were dramatically different from that of soils. In plants, for example, there was a marked shift toward lesser chlorinated congeners with a marked decrease in more chlorinated congeners. Taken together with the very low concentrations of total PCBs in plants relative to soil, these data are consistent with the fact that PCBs are not readily translocated into above-ground plant tissue. While it is possible that some of the PCBs in the plant tissue could be due to deposition of PCB-containing silt and particulates during times of inundation, the most likely mechanism is aerial deposition of lighter, more volatile congeners followed by absorption in the waxy cuticle (*33*).

For shrews, there was a dramatic shift in PCB patterns compared to that of soil (Figure 3). The lesser chlorinated PCB congeners were noticeably diminished whereas there was a notable enrichment of PCBs 153, 180, 138, 118, and 99. A similar pattern was observed for small mammals excluding shrews (data not shown) and passerine samples, indicating that this phenomenon may occur with a diverse array of species, at least those species with a functional Ah-receptor-mediated pathway leading to inducible cytochrome P450 enzyme activity and therefore greater metabolic capabilities.

One way to evaluate the potential role of metabolism on the relative differences in congener patterns in a food web is to group PCB congeners by structural features that are

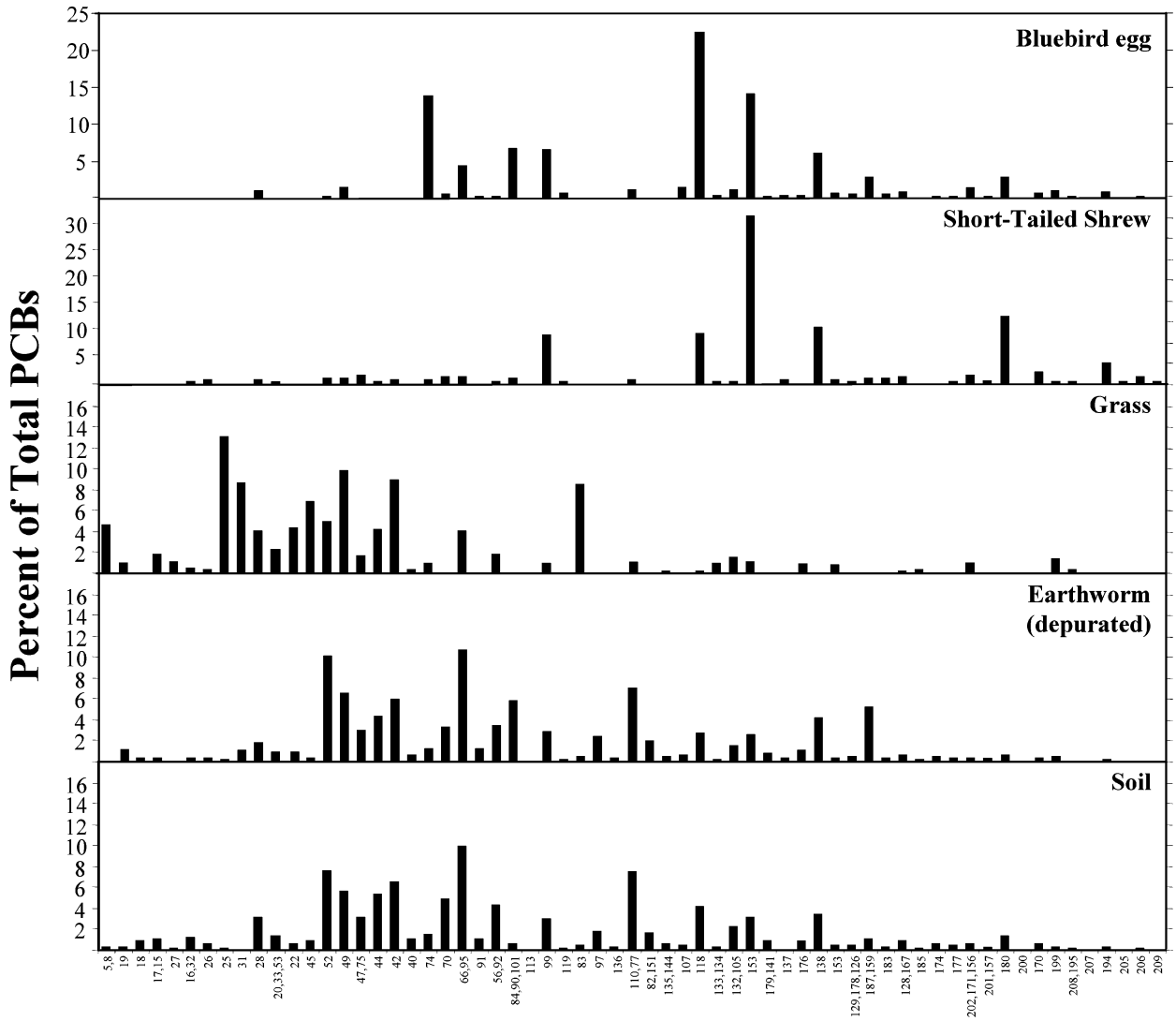

FIGURE 2. PCB congener pattern for representative samples of soil, grass, depurated earthworm, short-tailed shrews, and bluebird eggs collected from the former Trowbridge impoundment. Data (expressed as a weight percent relative to total PCBs) are from Trowbridge grid 1 in 2000.

related to potential susceptibility to catabolic metabolism (*34*−*35*). For example, many species of vertebrates are capable of enzymatically modifying congeners with adjacent unsubstituted meta and para carbons (i.e., lacking chlorines in these positions). Some species, including some marine mammals, can also enzymatically modify congeners with adjacent unsubstituted ortho and meta carbons (*36*). Such congeners can potentially be hydroxylated and excreted. If one evaluates the ratio of congener concentrations in earthworms from Trowbridge to that of colocated soil, often termed the biota−soil accumulation factor (BSAF), the ratio for the most abundant congeners ranged from 0.2 to 0.7, regardless of ortho-, meta-, and para-substitution patterns, with the exception of the coeluting pair of PCB 159/187 (Figure 3). In contrast, there were considerable differences in BSAFs among congeners for shrews. For example, average concentrations of PCB congeners with adjacent unsubstituted meta and para carbons (groups C and D in Figure 3) were diminished in shrews relative to soils, whereas congeners were generally stable or enriched with no adjacent unsubstituted meta and para sites (groups A and B in Figure 3). Thus, shrews, which occupy trophic positions higher up on the food chain and have relatively great metabolic capacity, appear capable of metabolizing certain congeners (e.g., generally those with adjacent unsubstituted meta and para carbons). This has been shown previously in aquatic systems and selected terrestrial species (*34*, *36*−*37*), but to our knowledge this has not been demonstrated in a complex terrestrial food web.

In general, it is not valid to apply a BSAF or BMF to transfer TEQs from one trophic level to another. This is because TEQs include a fractional contribution from several congeners that have unique toxicokinetic profiles. For this reason, each individual PCB congener needs to be corrected not only for its relative toxic potency but also its accumulation potential. In particular, PCB congeners 77 and 81, which may account for a substantial portion of the predicted avian TEQ concentration, are much more susceptible to metabolism than other congeners such as PCB congeners 126 and 169 (*11*, *37*−*39*). Even when such toxicokinetic differences are accounted for, there remains additional uncertainty regarding WHO avian TEFs. Recent work by Custer et al. (*13*) calls into question whether TEFs developed for PCBs are appropriate to predict effects in birds. For example, on the basis of tree swallow studies on the Woonasquatucket River, Custer et al. (*13*) derived a LD_{50} concentration of 1700 pg/g of TEQs in field-collected tree swallow eggs (primarily due to TCDD). However, if one compares this LD_{50} to concentrations of TEQs (calculated from PCBs) between 1730 and 12700 pg/g ww in tree swallow eggs from the Hudson River, then one would expect considerable population-level effects due to mortality. However, there were minimal effects on subtle endpoints at

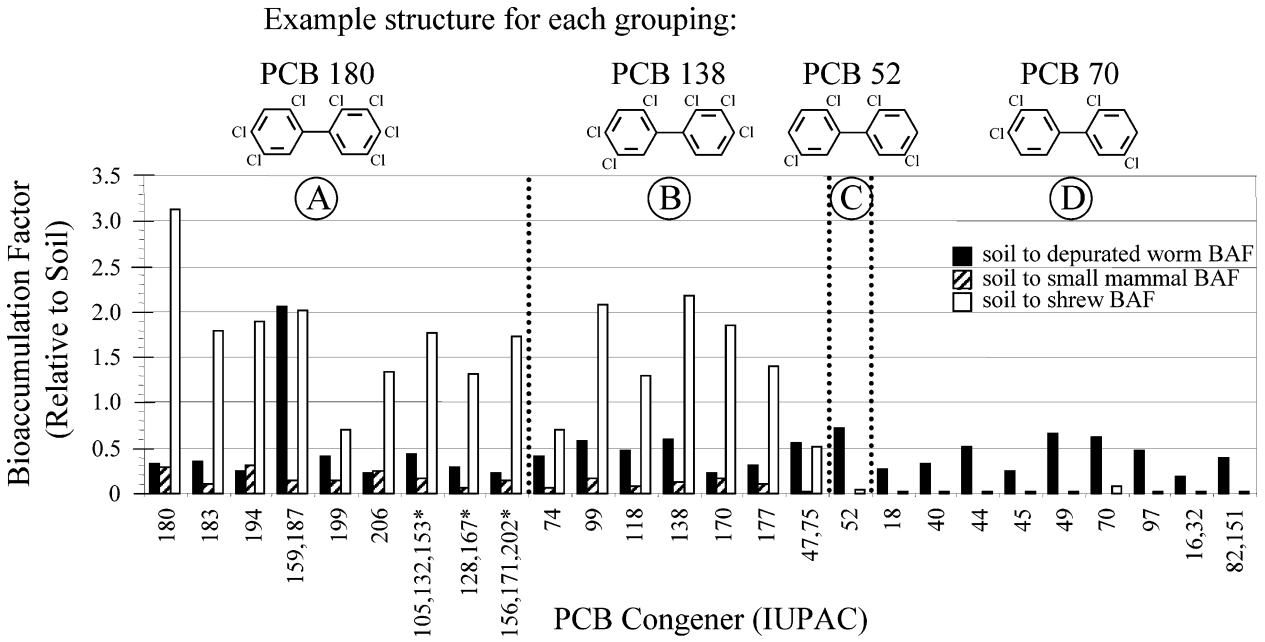

FIGURE 3. Relative accumulation of PCB congeners from soil to earthworms, shrews, and small mammals (excluding shrews) from the former Trowbridge impoundment (TB). Average PCB congener concentrations were adjusted to organic carbon content in soil and percent lipid in biota. PCB congeners are grouped as follows based on structural similarities: group A, no adjacent unsubstituted ortho−meta or meta−para sites; group B, adjacent unsubstituted ortho−meta but not meta−para sites; group C, adjacent unsubstituted meta−para but not ortho−meta sites; group D, adjacent unsubstituted ortho−meta and meta−para sites. The asterisk indicates that these coeluting congeners include congeners from both group A and group B.

TEQ concentrations (based on PCBs) in tree swallow eggs from the Hudson River (*40*). In other words, on the basis of this one comparison, a concentration of TCDD may not be toxicologically equivalent to the same concentration expressed as TEQs calculated from avian TEFs when PCBs contribute substantially to the calculated TEQs.

The relative potency of a PCB congener mixture can be calculated by dividing the concentration of TEQs (ng TEQs/kg) by the concentration of PCBs (mg PCBs/kg) in the same sample. The ratio of such relative potencies among different trophic levels is a useful measure of how the relative potency changes at each trophic level (*38*). Taken together with the BMF for total PCBs, a holistic picture can be developed that shows how both total PCB concentrations and dioxin-like potency of the PCB congener mixture changes by trophic level (Figure 4). From this analysis, it is clear that at TB there is a general reduction of relative potency (e.g., less than unity) at most trophic levels regardless of whether PCBs are biomagnified or not. For example, there is an apparent biomagnification of total PCBs going from terrestrial invertebrates to shrews (BMF = 16) whereas the relative potency ratio is only 0.23. For this example, the reduction in relative potency in shrews is, in part, due to lower concentrations of PCB 77, a congener that has been found to be susceptible to metabolism (*11*). One exception was for soil to terrestrial invertebrates, which is understandable since terrestrial invertebrates have a relatively low metabolic capacity. Another exception was the trophic transfer from adult robins to great horned owl eggs, in which there was an increase in both relative potency and in total PCB concentration. Since it is unclear how much of the great horned owl diet may consist of robins and similar passerine species, this apparent BMF may be an artifact. Also, since great horned owl samples are more limited in number and difficult to obtain compared to other sample types, the conclusions that have been drawn for this sample type are relatively limited.

Finally, in ecological risk assessments there is often a desire to predict concentrations of TEQs from total PCB data. This desire stems from the general thought that toxicity is better

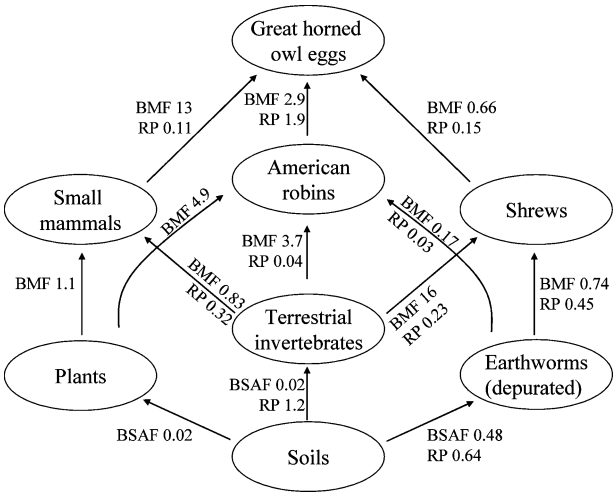

FIGURE 4. Lipid-normalized biota−soil accumulation factors (BSAFs), biomagnification factors (BMFs), and relative potency ratios (RPs) of the PCB congener mixtures at each trophic level using data from the former Trowbridge impoundment (TB).

correlated to TEQs than PCBs. However, there is often a lack of appropriate congener-specific data due to cost or other constraints at PCB-contaminated sites. EPA guidance suggests that for a given site it may be cost-effective and appropriate to analyze a subset of site-related samples for both total PCBs and PCB congeners to derive a correlation from which concentrations of TEQs may be estimated (*8*). Therefore, we evaluated the relationship between concentrations of PCBs and avian TEQs. While there was a general trend, as expected, in which concentrations of TEQs increased with total PCBs, this relationship was rather poor ($R^2 = 0.13$ using samples from TB and $R^2 = 0.059$ using samples from FC) when evaluated across all sample types. If one restricts the comparison among discrete sample types (using data from TB), then the correlation improves somewhat for certain sample types such as passerine adults ($R^2 = 0.50$), small

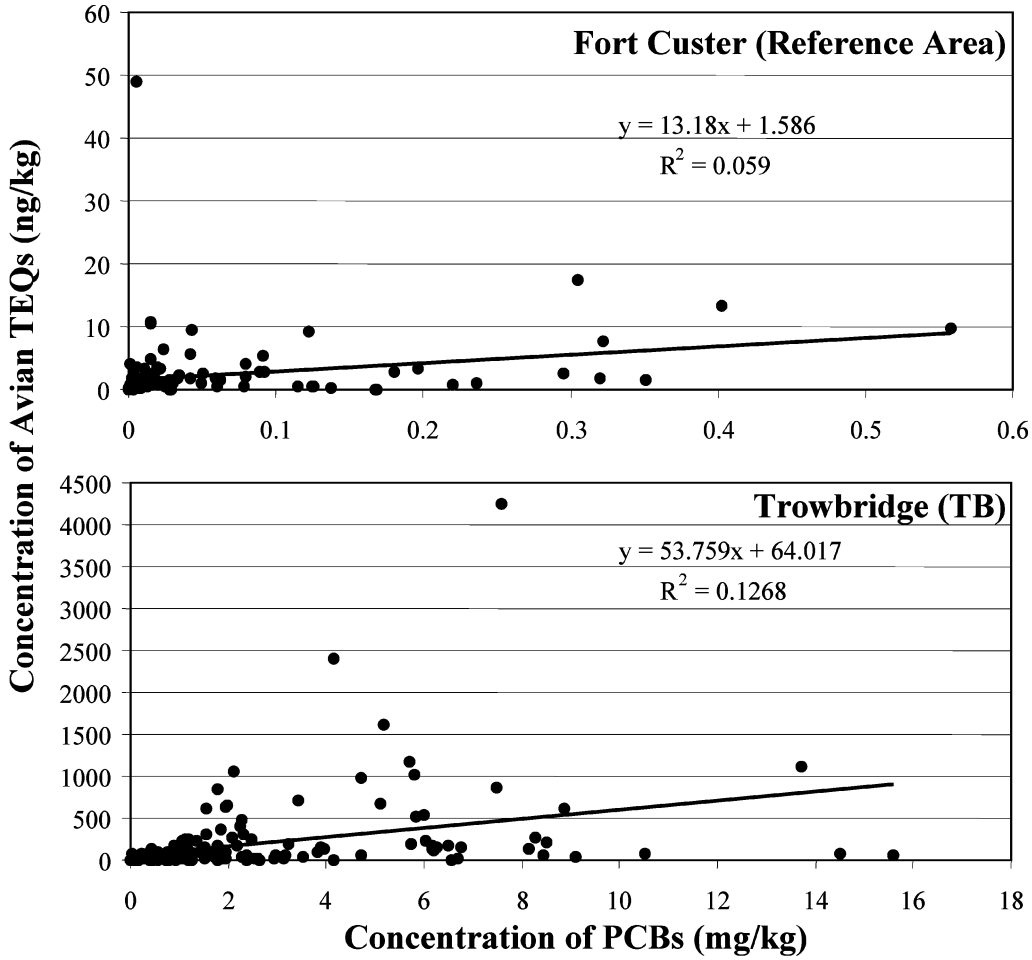

FIGURE 5. Scatter plot of PCB and avian TEQ concentrations for all individual samples from Fort Custer (top panel, 131 samples) and the former Trowbridge impoundment (lower panel, 173 samples). Concentrations are based on dry weight for soils and wet weight for biota.

mammals ($R^2 = 0.40$), terrestrial invertebrates ($R^2 = 0.49$), and worms ($R^2 = 0.42$), but the correlation was relatively poor for sample types such as soil ($R^2 = 0.16$), shrews ($R^2 = 0.0012$), and passerine nestlings ($R^2 = 0.0024$) and eggs ($R^2 = 0.0077$). Therefore, any attempts to estimate concentrations of TEQs from total PCB data should be evaluated carefully on a sample-specific basis.

On the basis of these results, if it is necessary to understand the concentration of TEQs at a site in a given sample type, then the most technically defensible approach would be to simply quantify individual PCB congeners. This would reduce uncertainty relative to estimating TEQ concentrations from total PCB data. However, the reduction in uncertainty would have to be weighed along with considerations of budgetary constraints, data quality objectives, and risk management options. Depending on the intended use of the data (e.g., delineation of the nature and extent of contamination, source evaluation, exposure assessment, and/or risk characterization), several factors should be evaluated to balance needs for information gained from congener-specific PCB analysis relative to uncertainty reduction and cost-effectiveness. For example, in the cases of nature and extent evaluation and screening-level ecological risk assessments, there may be little need to conduct congener-specific analysis when total PCB quantification can be conducted at a fraction of the cost and be sufficient to achieve the objectives. However, if there are multiple PCB sources that may need to be evaluated or if there is a relatively great likelihood of wildlife exposure, then congener-specific analysis of at least a subset of samples would be advisable. On the basis of the analyses of how well (or poorly) concentrations of TEQs relate to concentrations of total PCBs, it may be advisable to analyze all wildlife samples with congener-specific analysis. Finally, in the case of relatively rare samples of certain receptor tissues (e.g., peregrine falcon eggs, etc.), it is highly recommended that a congener-specific analysis with ultralow detection limits for coplanar PCB congeners be performed to maximize the information gained from such a limited sample.

In conclusion, concentrations of PCBs were lower in biota than those the in soil from the KRAOC although there was a modest biomagnification of PCBs from certain lower trophic level biota to higher trophic levels (e.g., terrestrial invertebrates to shrews, small mammals to great horned owls, etc.). Furthermore, environmental weathering of PCBs in the terrestrial food web of the KRAOC led to a decrease in the relative potency of PCBs (expressed as mg TEQs/kg PCBs) from soil to most biota. Taken together, these data suggest that differential accumulation of PCB congeners in the terrestrial food web can be explained by congener-specific differences in bioavailability from soil, exposure pathways, and metabolic potential of each of the food web components.

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Supporting Information Available

Congener-specific data for the Trowbridge and Fort Custer sites (all grids combined). This material is available free of charge via the Internet at http://pubs.acs.org.

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