BIOACCUMULATION OF POLYCHLORINATED BIPHENYLS FROM SEDIMENTS TO AQUATIC INSECTS AND TREE SWALLOW EGGS AND NESTLINGS IN SAGINAW BAY, MICHIGAN, USA

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(Received 19 December 1996; Accepted 15 July 1997)

Abstract—Sediments in the Saginaw Bay region of the Great Lakes contain concentrations of polychlorinated biphenyls (PCBs) that may adversely affect biotic species in various trophic levels. In this study we collected and analyzed sediments, benthic invertebrates, tree swallow eggs, and nestlings to evaluate linkages between PCBs in sediments and at various trophic levels in the Saginaw River, Michigan, USA. Our results indicate that patterns of relative concentrations of PCB congeners change with trophic level, specifically from sediment to invertebrates and from tree swallow eggs to nestlings. However, if biota–sediment accumulation factor (BSAF) values are based on only the non- and mono-ortho-substituted PCB congeners or 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEq), calculated BSAF values are close to those predicted by fugacity theory. The use of site-specific BSAF values and reference doses for toxic effects in wildlife can be used to derive sediment quality criteria (SQC) that are protective of wildlife at the top of the sediment-based food chain. The threshold concentration of TEq in sediments that would protect sensitive avian species at the same trophic level as tree swallows was calculated to be $1.5 \times 10^{-1}$ TEq/g total organic carbon. Based on this value and the BSAF determined for tree swallow nestlings, the hazard quotient for sediments in this area was determined to be 0.7. This indicates that current concentrations of TEq due to PCB congeners in the sediments should be below the threshold for adverse effects on tree swallows. The uncertainty in the concentrations of PCB congeners in the sediments was approximately a factor of 2, which determined the degree of resolution that could be obtained from the observations made in this study.

Keywords—Biota–sediment accumulation factor Bioaccumulation Benthic invertebrates Birds Fugacity

INTRODUCTION

Although polychlorinated biphenyls (PCBs) are no longer manufactured in North America and releases to aquatic systems have been greatly reduced [1], some locations in the Great Lakes region, particularly rivers [2] and harbors [3,4], have sediments that contain concentrations of PCBs that might be of toxicological significance and remain a concern [5,6]. Historically, the Saginaw River watershed (Michigan, USA) has been contaminated with PCBs from various sources [7,8]. The region has been shown to contain substantial concentrations of PCBs in sediments [9,10], water, and biota [8,11,12]. Current issues involving PCBs in the Saginaw Bay system center on remediation and restoration [9]. The design of effective remediation and restoration plans is dependent on judging the degree to which PCB-contaminated sediments need to be remediated to achieve restoration goals. Thus, a current issue relative to in-place pollutants, such as PCBs, is whether they are available to biota and how to estimate the potential of such complex mixtures to be accumulated in higher trophic levels [13,14] such that sediment quality criteria (SQC) protective of the highest trophic levels can be established.

Several methods of predicting the availability and accumulation potential of sediment-bound contaminants to organisms at higher trophic levels have been proposed [11]. These methods include food chain models based on fugacity [15–17] and simple empirical methods in which proportionality factors are used, referred to as biota–sediment accumulation factors (BSAFs) [18–20]. It should be noted that empirical BSAF values are not based on fugacity theory. These values implicitly consider the disequilibrium that exists, or can exist, between the sediment and pelagic species [18]. When applied to aquatic species such as benthic invertebrates, BSAFs are defined as ratios of concentrations of compounds on a lipid-normalized basis to organic carbon-normalized concentrations of the same compounds in sediments [19,20]. When predicting higher-order accumulations such as into birds that eat aquatic organisms, similar ratios are used and are referred to as biomagnification factors (BMFs) [13]. Although the BSAF–BMF method can be empirical in nature [18,20], it also could be based on fugacity theory through the use of several assumptions, including that the system is at steady state. A further assumption under both theories is that the accumulation ratios (BSAFs and/or BMFs) are constants that can be applied from one location to another [13,21,22]. The research presented here is a test of the utility of the BSAF–BMF approach to predict accumulation of PCBs to the top of a sediment-based food chain.

Polychlorinated biphenyls are a complex mixture of congeners of differing chemical and physical properties and toxic potencies, with the stereochromically more planar non- and mono-ortho-substituted congeners having the greatest aryl hydrocarbon (Ah) receptor-mediated activity [23]. For this rea-
son, if total PCB concentrations are used in risk or hazard assessments, an assumption of the fugacity-based BSAF–BMF methodology is that the pattern of relative concentrations of individual congeners does not change as a function of space, time, or trophic level [24,25]. In this study, we determined the patterns or relative concentrations of individual congeners, as well as total PCB concentrations, among trophic compartments and determined whether toxic potentials of PCB mixtures change as a function of trophic level. Concentrations of PCBs were measured in sediments, emergent aquatic insects (primarily chironomidae), and eggs and nestlings of tree swallows (Tachycineta bicolor) from sites within the Saginaw River watershed. In addition, the BSAF–BMF method was used in conjunction with reference doses to calculate sediment PCB concentrations that are theoretically protective of tree swallows, based on estimates of the toxicity of PCBs or 2,3,7,8-tetrachlorodibenzop-dioxin (2,3,7,8-TCDD) equivalents (TEqs) to other bird species [26,27].

Passerine species have been used as indicators of local organochlorine contamination [28]. Specifically, accumulation of PCBs by nestling tree swallows has been modeled, and their use as integrative biomarkers of local organochlorine contamination has been reported [11]. Tree swallows have utility as integrative monitors of the bioavailability of contaminated sediments because, if they occupy nest boxes placed over contaminated sediments at locations that are remote from terrestrial areas, they feed almost exclusively on insects that emerge from juvenile stages that have lived in proximity to the sediments [11,29,30].

**MATERIALS AND METHODS**

**Sample sites and collection**

Samples of sediment, emergent insects, tree swallow eggs, and tree swallow nestlings were collected in 1992 within the Saginaw Bay watershed (Fig. 1). Tree swallow eggs were chosen at random from nests containing five or more eggs (maximum of two eggs per nest). Nestlings were collected from nests and euthanized by asphyxiation with CO2 at an age of 15 d. Details of methods and locations of collections were described previously [11,31]. Diet and bioenergetics of the tree swallow nestlings have also been discussed in detail elsewhere [11] and are beyond the scope of this article.

**Extraction and clean-up**

Sediment (10 g wet weight) and invertebrate (1–10 g wet weight) samples were Soxhlet extracted (16 h) using 250 ml of acetone: hexane (1:1). Composites of tree swallow eggs (10 g wet weight) and nestlings (10 g wet weight) were homogenized and ground with five times their weight of anhydrous sodium sulfate, then extracted with 200 ml of dichloromethane. The feet, beaks, and wings of the nestling were removed before homogenization. Lipid contents were determined gravimetrically by evaporating to constant weight a 1% (vol) portion of the extract in a preweighed aluminum weighing dish. Pesticides, lipids, and interfering compounds were removed from the sample matrix via an acid-base silica gel column composed of 1 cm sodium sulfate over 1 g of 40% H2SO4/silica gel (w/w), 5 g silica gel, 1 g 33% KOH (1 M)/silica gel, and 1 cm sodium sulfate in a 1-cm (inner diameter) reservoir column. Polychlorinated biphenyls were eluted with 50 ml of 0.5% benzene in hexane. The extract was evaporated via rotary evaporation and nitrogen evaporation to a final volume of 0.5 ml. Polychlorinated biphenyl 30 (47 ng) was added as an internal standard, and the extract was adjusted to a final volume of 1.0 ml. Silica gel (Silica Gel 60, 70-230 mesh, Sigma Chemical Company, St. Louis, MO, USA) was activated at 130°C for 12 h. All solvents used in this procedure were pesticide grade and were obtained from Burdick and Jackson (Muskegon, MI, USA).

**Instrumental quantification**

Concentrations of major PCB congeners, mostly di-ortho-substituted, were determined using a Perkin-Elmer Autosystem Gas Chromatograph (GC) equipped with an autosampler, split/splitless injector, and electron capture detector (ECD). The injector was operated in splitless mode at 250°C, and the detector was held at 350°C. A DB-5 J&W Scientific, Palo Alto, CA, USA) (30 m × 0.25 mm inner diameter, df, = 0.25 μm) chromatographic column was used to separate the PCBs into 84 peaks, which accounted for 110 PCB congeners. The GC oven was ramped from 120°C (1 min hold) at 2°C/min to 260°C and held for 5 min. Quantification was based on relative response factors calculated from a calibration mixture of Aroclors 1242:1248:1254:1260 (1:1:1:1) and the internal standard (PCB 30). Total concentrations of PCBs (PCBtotal) were calculated by summing the concentrations for individual PCB congeners. Estimations of the original Aroclor composition in selected collections were calculated using COMSTAR, a multiple-regression program for quantitating PCB mixtures as linear combinations of Aroclors [32].

Non- and mono-ortho-PCB congeners were measured in the bulk PCB extract after concentrating the extracts to a final volume of 100 μl. Sample extracts were injected in splitless mode onto a selective GC column, Chrompack CP SIL 5/C18 (100 m × 0.25 mm inner diameter, 0.1 μm film) in a Hewlett Packard (Palo Alto, CA, USA) 5890 Series II+/5972A Gas Chromatography–Mass Selective Detection (GC–MSD) system. The GC oven temperature was held initially at 90°C for 3 min, ramped at 20°C/min to 220°C, held for 5 min, then ramped at 1.2°C/min to 270°C. The MSD was operated in selected ion monitoring mode, in which the three most abundant isotopic peaks for each homologue group were monitored. The GC–MSD was calibrated with a custom PCB mixture (Ultra Scientific, North Kingstown, RI, USA) via a four-point calibration curve. Calculations for quantification of analytes.
were made with Hewlett Packard Chemstation software. Manual integration was necessary for peaks near the detection limit.

2,3,7,8-Tetrachlorodibenzo-p-dioxin equivalents were calculated as the sum of the products of concentrations of individual non- and mono-ortho congeners and their potency factors (toxic equivalency factors [TEFs]), relative to 2,3,7,8-TCDD. Toxic equivalency factors used for these calculations were derived from induction of ethoxyresorufin-O-deethylase activity in the H4IIE rat hepatoma cell line (Appendix) [33,34].

### RESULTS AND DISCUSSION

Average lipid-normalized PCBtotal concentrations were not different among the invertebrates, eggs, or nestlings (Table 2); the average total organic carbon (TOC)-normalized PCBtotal in sediments was about one order of magnitude less than tissue values. The variation within sample matrices was great because samples were taken from different sites within the test region. For example, the range of PCBtotal, as quantified by GC–ECD, for sediment was <500 to 7,700 ng PCBtotal/g TOC. This resulted in a mean PCBtotal value of 1,700 ng PCBtotal/g TOC with a relative SD of 150%. The sample size was not sufficient to test for differences among sampling sites. Because of the heterogeneous nature of PCB concentrations in the sediments, the resolution of calculations that used absolute concentrations of PCBs was deemed to be approx. 2.0. For instance, when measuring ratios of PCBs among trophic levels, the values needed to be at least twofold different to be deemed significant.

Predicted Aroclor compositions (relative proportions) were similar among sample matrices, which indicates similar sources within the region (Table 1). The average lipid-normalized concentrations of PCBtotal for invertebrates, tree swallow eggs, and nestlings were not different at the resolution of calculations that used absolute concentrations and lipid-normalized concentrations in the tissues of the biota. Furthermore, this observation indicates that the changes in relative concentrations of individual PCB congeners did not have a great influence on the total mass of PCBs predicted to occur in tissues of higher trophic levels. In addition, these results suggest that PCBtotal values in the tissues of the tree swallow eggs and nestlings were near steady state.

#### Pattern recognition

Principal components analysis was performed on the PCBtotal-normalized concentrations of individual congeners (Fig. 2). Forty-seven percent of the variance was explained by principal components 1 and 2. The results of the principal components analysis support the alternative hypothesis that the pattern of relative concentrations of PCB congeners in sediments was different from that in tissues of organisms. This indicates that patterns of relative concentrations of PCB congeners in sediments are different from those in higher trophic levels due to processes such as weathering, bioaccumulation, and metabolic processes. The tree swallow nestlings were differentiated from the eggs and invertebrates in the two principal components. Reasons for this are likely differences in the metabolic processes in the nestlings compared to the eggs. The nestlings undergo a period of rapid biological/metabolic development in which lipid stores and new lipid sources are rapidly biotransformed into thermal energy and cellular growth [11]. The adult female tree swallow, on the other hand, may rapidly process new lipids from the food source (invertebrates) into the production of egg lipids without many of the biotransformation processes that allow metabolism of the PCB congeners, thus producing eggs that have similar relative ratios of PCB congeners as the food source.

Environmental weathering changes the relative concentrations of PCB congeners due to differential solubilities, volatilities, and sorption coefficients [38]. In addition, other studies have shown that metabolism by microorganisms [39] and animals [40,41] can cause relative proportions of some congeners to increase while others decrease [41,42]. Thus, metabolic differences between organisms at successive trophic levels may result in distinct biotransformation of individual PCB congeners. The separation of the nestlings in the principal components plot is, perhaps, an indication that this indeed occurs. Concentrations of selected congeners that contribute significant proportions of the mass of Aroclor 1242, 1248, 1254, and 1260 are provided (Table 2).

Mean ratios of lipid-normalized non- and mono-ortho-substituted congeners were not significantly different among the egg/invertebrate and nestling:egg trophic level ratios (Fig. 3); however, they were different from the invertebrate/sediment mean ratio (lipid normalized vs TOC normalized). Concentrations of PCBs 77 and 81 were less in eggs than in invertebrates. This might be due to differential metabolism between birds and invertebrates [41,43]. Alternatively, congeners 126, 167,
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Table 2. Mean polychlorinated biphenyl (PCB) concentrations for selected congeners (gas chromatography–electron capture detection [GC–ECD] analysis)

<table>
<thead>
<tr>
<th>PCB congener</th>
<th>Invertebrates (ng/g lipid)</th>
<th>Tree swallow eggs (ng/g lipid)</th>
<th>Tree swallow nestlings (ng/g lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>n</td>
</tr>
<tr>
<td>17</td>
<td>1.1E + 02</td>
<td>2.0E + 02</td>
<td>6</td>
</tr>
<tr>
<td>16 + 32b</td>
<td>6.8E + 01</td>
<td>1.0E + 02</td>
<td>9</td>
</tr>
<tr>
<td>28 + 31</td>
<td>3.3E + 02</td>
<td>3.1E + 02</td>
<td>9</td>
</tr>
<tr>
<td>42</td>
<td>1.1E + 03</td>
<td>1.1E + 03</td>
<td>9</td>
</tr>
<tr>
<td>136</td>
<td>4.3E + 03</td>
<td>2.6E + 03</td>
<td>9</td>
</tr>
<tr>
<td>77 + 110</td>
<td>7.7E + 02</td>
<td>8.7E + 02</td>
<td>9</td>
</tr>
<tr>
<td>151</td>
<td>1.4E + 02</td>
<td>1.6E + 02</td>
<td>9</td>
</tr>
<tr>
<td>123 + 149</td>
<td>4.9E + 02</td>
<td>5.0E + 02</td>
<td>9</td>
</tr>
<tr>
<td>118</td>
<td>5.7E + 02</td>
<td>5.2E + 02</td>
<td>9</td>
</tr>
<tr>
<td>153 + 132</td>
<td>6.2E + 02</td>
<td>5.1E + 02</td>
<td>9</td>
</tr>
<tr>
<td>138</td>
<td>7.0E + 02</td>
<td>5.8E + 02</td>
<td>9</td>
</tr>
<tr>
<td>182 + 187</td>
<td>2.8E + 02</td>
<td>2.4E + 02</td>
<td>9</td>
</tr>
<tr>
<td>174</td>
<td>1.1E + 02</td>
<td>9.3E + 01</td>
<td>9</td>
</tr>
<tr>
<td>180</td>
<td>1.3E + 01</td>
<td>1.1E + 01</td>
<td>9</td>
</tr>
<tr>
<td>PCBtotalc</td>
<td>1.9E + 04</td>
<td>1.9E + 04</td>
<td>9</td>
</tr>
</tbody>
</table>

*a E = \times 10^p*.

b 16 + 32 indicates coeluting peaks. They are integrated and quantified as one peak.

c PCBtotal values are the sum of 81 quantified peaks in the GC–ECD chromatogram.

and 156, perhaps because of their more fully occupied meta
tpositions, do not appear to be metabolized significantly in
different biota [44].

Overall, the differences in congener patterns appear to sig
nify a departure from fugacity-based BSAF–BMF theory,
which, as indicated earlier, assumes that relative concentrations

of individual congeners do not change as a function of space,
time, or trophic level.

2,3,7,8-Tetrachlorodibenzo-p-dioxin equivalents

Among the critical toxicants to which birds in the Great
Lakes region are exposed are not total PCBs but rather con
centrations of the congeners that are structurally similar to
2,3,7,8-TCDD [12,26]. 2,3,7,8-Tetrachlorodibenzo-p-dioxin
equivalents represent the total potential of the PCBs to cause
TCDD-like toxicity. The values represent a weighted average
of the concentrations of individual non- and mono-ortho-sub-
stituted PCB congeners corrected for their relative potencies.
Lipid-normalized concentrations of TEq appear to increase
with trophic level (Table 3) for the biotic matrices; however,
of these, only the invertebrate–egg transfer is significant (p < 0.01). Additionally, the TOC-normalized TEq for the sediment
is significantly greater (p < 0.01) than the lipid-normalized
TEq in the invertebrates. For the samples analyzed in this
study, 87% (s = 3%) of the calculated TEq was contributed by
PCB 126.

The ratio between TEq in the sediments and that in inver-
tebrates is a function of bioavailability. The concentration of
TEq, on organic carbon- and lipid-normalized bases, decreases
by a factor of about 3.3 from the sediments to the invertebrates.
This may represent a measure of bioavailability of the non-
and mono-ortho-substituted congeners due to factors not ac-
counted for by organic carbon normalization. The organic car-on in sediments is not exactly the same as invertebrate lipids
[36], and it has been suggested that the correction factor from
sediment organic carbon to tissue lipids is approx. 1.7, with
lipid dissolving more solute than organic carbon in sediments
[37]. If the ratio of normalized concentrations from sediment
to invertebrate is corrected for this factor, a ratio of 1.9 is
calculated. Theoretically, this value should be 1.0. Thus, only
about half the mass of PCB in the sediment, normalized to
organic carbon, is available for equilibrium partitioning. That
is, the biologically available fraction is approx. 0.5. As indi-
cated above, the variation in concentrations of PCBs was such
that differences of less than a factor of 2 were not discernible.
Thus, it is not possible to conclude that there were effects on
bioavailability not accounted for by carbon normalization. The estimate of bioavailability is complicated somewhat by the fact that invertebrates may include sediment in their guts [45]. Thus, the ratio between the two compartments may be biased either up or down depending on the effect that this has on the fugacity of the system.

Comparison of calculated TEq values (Table 3) with PCB_{total} (Table 1) shows that while average PCB_{total} values do not change across trophic levels, the distributions of the congeners change significantly. Potency is defined as the ratio of TEq normalized to a PCB congener that contributes a significant proportion of the total PCB mass and does not selectively weather or degrade, such as PCB 153 (Table 4) [30]. The potency ratio (Eqn. 1), as used in this study, is defined as the quotient of TEq concentrations of adjacent trophic levels. Although Equation 1 gives the calculation to normalize to concentrations of congener 153, a similar calculation can be made with mass of PCB_{total} (Table 4). In this manner we can account for bioaccumulation among broad concentration ranges, samples, sample types, and biologically available fractions to focus on the change in toxic potential.

Potency ratio = \frac{(\text{TEq}_{tr2}/\text{PCB}_{153, tr2})}{(\text{TEq}_{tr1}/\text{PCB}_{153, tr1})} \tag{1}

where

PCB_{153, tr} = \text{concentration of PCB congener 153 in trophic level},

TEq_{tr} = \text{equivalent concentration of 2,3,7,8-TCDD in trophic level},

and

tr1 and tr2 = trophic levels 1 and 2, respectively.

No change in toxic potential from the egg to the nestling (potency ratio_{nestling/egg} = 1.0) was observed (Table 4). However, the potency changed by nearly a factor of 3 from the invertebrate to the egg (potency ratio_{egg/invertebrate} = 2.6). A potency ratio of 1.0 would be expected for the nestling/egg ratio since there was little opportunity for significant metabolism or accumulation of PCBs from the egg to the nestling. The change in potency was only slightly greater than the discriminatory power of two set by the variation in the data. For the initial trophic transfer, the adult bird accumulates, metabolizes, and transfers the organochlorines into the developing egg. The nestlings retain the compounds contained in the egg, the concentrations of which are diluted by growth, but also begin further accumulation through feeding [46]. A sharp apparent decrease in the toxic potential from the sediment to the invertebrates was observed (ratio = 0.01). As discussed above, this is probably due in part to the differences in bioavailability of the lipophilic compounds in the organic carbon on the sediment versus the lipid of the invertebrates. The relative proportion of those congeners that contribute the most to the toxic potential have been shown to increase with trophic level from sediments to birds [30,46]. The relative potency factors observed here are similar to those that can be calculated for tree swallow eggs and nestlings from Green Bay, Wisconsin, USA [29]. Using those data, we calculated relative potencies based on total PCBs of $1.6 \times 10^{-3}$ and $1.8 \times 10^{-2}$ for tree swallow eggs and $1.1 \times 10^{-5}$ for 16-d-old nestlings. The average of

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Table 3. Average 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEq) calculated from the average sum of non- and mono-ortho-substituted polychlorinated biphenyls (PCBs) (as listed in Table 1) and the resulting TEq ratios across trophic levels.

<table>
<thead>
<tr>
<th>Sample matrix</th>
<th>n</th>
<th>Sum non- + mono-ortho-PCBs</th>
<th>TEq</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ng/g lipid</td>
<td>s</td>
</tr>
<tr>
<td>Sediment*</td>
<td>5</td>
<td>$1.6E^{+3}$</td>
<td>$3.2E^{+2}$</td>
</tr>
<tr>
<td>Invertebrate</td>
<td>7</td>
<td>$5.5E^{+2}$</td>
<td>$4.5E^{+2}$</td>
</tr>
<tr>
<td>Egg</td>
<td>9</td>
<td>$1.1E^{+3}$</td>
<td>$5.6E^{+2}$</td>
</tr>
<tr>
<td>Nestling</td>
<td>7</td>
<td>$1.7E^{+3}$</td>
<td>$2.4E^{+3}$</td>
</tr>
</tbody>
</table>

* Sediment values are expressed as nanograms per gram of organic carbon.

$E = \times 10^n$. 

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Fig. 3. Ratios of polychlorinated biphenyl (PCB) congeners at one trophic level to the next lower trophic level. Horizontal lines in the plot indicate the mean ratio values: invertebrate/sediment, 0.51 ($s = 0.36$); egg/invertebrate, 1.9 ($s = 0.94$); and nestling/egg, 1.4 ($s = 0.30$). TOC = total organic carbon.
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Table 4. Relative concentrations ratios of congeners 153 + 132 to PCB_{total}, relative potencies of 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents normalized to either PCB 153 or PCB_{total}, and the corresponding potency ratios.

<table>
<thead>
<tr>
<th>Sample matrix</th>
<th>PCB 153 /PCB_{total}</th>
<th>Potency</th>
<th>Potency ratio(^a)</th>
<th>Potency</th>
<th>Potency ratio</th>
<th>Potency</th>
<th>Potency ratio</th>
<th>Enrichment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>0.014</td>
<td>4.7E-5</td>
<td>3</td>
<td>8.2E-5</td>
<td>5</td>
<td>6.7E-5</td>
<td>5</td>
<td>120</td>
</tr>
<tr>
<td>Invertebrate</td>
<td>0.032</td>
<td>4.7E-5</td>
<td>0.01</td>
<td>1.5E-6</td>
<td>0.02</td>
<td>5.3E-5</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Tree swallow egg</td>
<td>0.048</td>
<td>1.2E-4</td>
<td>2.6</td>
<td>5.9E-6</td>
<td>3.9</td>
<td>8.1E-5</td>
<td>1.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Tree swallow nestling</td>
<td>0.055</td>
<td>1.3E-4</td>
<td>1.0</td>
<td>7.1E-6</td>
<td>1.2</td>
<td>6.0E-5</td>
<td>0.8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\(^a\) Potency ratio calculated as described in Equation 1. The ratio is always the potency of the higher trophic level matrix divided by the potency of the matrix that is one trophic level lower.

\(^b\) Calculated as described in Equation 2.

\(\times 10^n\).

these potencies (1.5 \times 10^{-3}) is only 2.2 times greater than that of the Saginaw Bay tree swallow eggs and nestlings (6.6 \times 10^{-6}) and thus only slightly greater than the twofold discrimination power of the study.

Polychlorinated biphenyl 153 is often used for normalizing PCB data [17] because it is a major component of several technical PCB mixtures. It is a di-ortho-substituted hexachlorinated congener that does not have vicinal unsubstituted carbon atoms and is thus not significantly metabolized by most organisms. On a DB-5 chromatographic column, PCB 153 coelutes with PCB 132. The relative ratios of these two congeners are variable and depend on a number of factors, including metabolic processes among trophic levels or specific species [47]. Polychlorinated biphenyl 132 may be metabolized, whereas PCB 153 is not. Additionally, other PCB congeners are metabolized, which ultimately results in the relative ratio of PCB 153 increasing with trophic level (Table 4). The effect of this increase is that use of the PCB 153 + 132 peak for normalization may underestimate the potency, particularly if there are significant metabolism differences between tr1 to tr2 (Eqn. 1). However, the error caused by this effect is small because the ratio of the PCB 153 + 132 peak to PCB_{total} does not change drastically among trophic levels (Table 4). We have reported the relative potencies normalized to both the mass of PCB 153 + 132 and PCB_{total} congeners (Table 4). Whichever convention is used, the potential bias of each normalization method must be considered, particularly when comparing data from different sources. Ratios of the relative potencies among trophic levels demonstrated a decrease in the relative toxic potency from sediment to invertebrates but an increase between invertebrates and tree swallow eggs (Table 4).

The relative enrichment of TEq with respect to the original Aroclor mixture in the same trophic level can also be calculated (Table 4). Enrichment was defined as the PCB 153-normalized ratios of TEq concentrations in samples to concentrations of the Comstar-weighted original Aroclor TEq calculated based on the PCB congener distribution-weighted estimates of the relative proportions of Aroclors predicted by COMSTAR (Eqn. 2). This ratio provides a measure of the extent of change of the relative toxic potency of the PCB mixture in the environment, measured as TEq increases from the original combination of technical Aroclor mixtures that were released into the environment.

Enrichment

\[
\text{Enrichment} = \frac{(\text{TEq}_{\text{sample}} / \text{PCB}_{153,\text{sample}})}{(\text{TEq}_{\text{Aroclor}} / \text{PCB}_{153,\text{Aroclor}})} \quad (2)
\]

where

TEq_{\text{sample}} = 2.3,7,8-TCDD toxic equivalents contributed by PCB in the sample,

TEq_{\text{Aroclor}} = 2.3,7,8-TCDD toxic equivalents from COMSTAR-weighted original Aroclor contributions,

PCB 153_{\text{sample}} = concentration of PCB 153 in the sample, and

PCB 153_{\text{Aroclor}} = concentration of PCB 153 from COMSTAR-weighted original Aroclor contributions.

Enrichment of TEq for invertebrates (Table 4) indicates that little change occurred in the PCB composition due to weathering or metabolic processes. However, for tree swallow eggs and nestlings, enrichment did occur. This is likely a result of metabolic processes that selectively dechlorinate and/or excrete some congeners while allowing others, primarily the more Ah-active non- and mono-ortho-substituted congeners, to accumulate [41,48]. The relative enrichment of TEq for sediments is 120, which is 15 to 80 times greater than the apparent relative enrichment for biota in the trophic levels above the sediment and much greater than the twofold factor defined as the approximate discrimination factor.

Biota–sediment accumulation factor values

The BSAF has been proposed as an empirical relationship to predict the lipid-normalized concentrations of residues from the TOC-normalized concentration of the same residue in sediments [13,20,49]. The BSAF approach has been proposed for use as a regulatory tool in risk assessment methodologies involving contaminated sediments [13,50] and in conjunction with an appropriate reference dose to calculate SQC that are protective of wildlife [13].

Biota–sediment accumulation factor values varied, depending on whether they were calculated based on PCB_{total}, the sum of non- and mono-ortho-substituted PCBs, or TEq (Table 5). The BSAF values calculated based on PCB_{total} were between 8.8 and 11, while those based on non- and mono-ortho-substituted congeners ranged from 0.3 to 1.1 (Table 5). The BSAF is operationally defined and can be site and species specific [51]. The actual BSAF values measured are dependent on the chemophysical properties of both the residue and sediments. Although TOC is similar among sediments, there are qualitative differences that are not accounted for in the BSAF. In addition, the relative importance of TOC and inorganic properties and size of sediment particles.
Table 5. Biota–sediment accumulation factor (BSAF) values for each matrix based on the sum of polychlorinated biphenyls (PCBs), the sum of the non- and mono-ortho-substituted PCB congeners, and 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEq) (each value represents the ratio of the lipid-normalized concentration in tissue divided by the organic carbon normalized concentration in sediments)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>PCB$_{\text{total}}$</th>
<th>Non- + mono-ortho-PCBs</th>
<th>TEq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invertebrates</td>
<td>11</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Tree swallow eggs</td>
<td>8.8</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Tree swallow nestlings</td>
<td>9.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

can influence BSAF values. Also, duration of the presence of the residue in the sediment and exposure of biota to the sediments can influence the BSAF value, particularly for super-hydrophobic compounds that take a long time to come to steady state with both the sediment and benthic matrices [52]. Finally, composite samples of emergent invertebrates integrate the overall exposure of organisms to an area in which actual concentrations of residues, such as PCBs, type of sediment, and TOC content can be heterogeneous. Thus, in calculating a BSAF, relatively great variations in values can be observed if a limited number of samples of TOC-normalized sediment residue concentrations are used to estimate the denominator of the BSAF. This was the case in our study. The average TOC-normalized PCB$_{\text{total}}$ concentration in sediments was 1.7 µg PCB/g TOC ($s = 2.6$ µg PCB/g TOC) with a range of more than 34-fold between the least and greatest values. If the maximum value were used instead of the average value, the BSAF would be approx. 1.0. Thus, the anomalously great value of the BSAF for PCB$_{\text{total}}$ is probably due to this sort of variation. Thus, based on this type of sensitivity analysis, a range of as much as 35-fold would be expected in BSAF values calculated in this manner. The use of BSAF values in risk assessments assumes that these values do not vary among locations or that an overall average value can be calculated for a region. Although this is not necessarily an invalid assumption, the range of BSAF values must be considered in addition to the average in interpreting the results of risk assessments. As with variation in residue concentrations, some level of resolution needs to be defined for the use of BSAFs. For our study in the Saginaw Bay system, this would be approx. 35.

Biota–sediment accumulation factor values for PCB$_{\text{total}}$ were all greater than would be expected based on fugacity theory. This may be related to the contribution of PCBs in sediments within the guts of the invertebrates. When BSAF values were based on the sum of non- and mono-ortho-substituted PCB congeners or TEq, BSAF values were less than or equal to 1.1 (Table 5), with the range of estimated BSAF falling within the previously defined twofold level of resolution for this study. The discrepancy between BSAFs based on PCB$_{\text{total}}$ and those based on the sum of non- and mono-ortho-PCBs is likely contributed by analytical method biases between the instrumental analyses used in this study. If the mean sediment PCB$_{\text{total}}$ values are an underestimate of the “true” value, BSAFs, as well as the calculated potencies, based on this value will be higher than predicted by theory.

Biota–sediment accumulation factor values have been reported to range from 0.1 to 10 for benthic invertebrates [53]. The BSAF values observed for the distribution of PCB$_{\text{total}}$ between sediments and infaunal invertebrates can range by up to two orders of magnitude, but a global average value of 1.7 has been suggested for use in risk assessments where BSAF values have not been determined for a particular site [54]. For example, BSAF values for accumulation of PCBs from marine sediments by infaunal organisms such as mollusks (Mercenaria mercenaria) and polychaetes (Nephtys incisa) ranged from 1.7 to 4.6, depending on the PCB congener [51], while BSAFs for accumulation of PCB 153 by the mayfly (Hexagenia limbata) ranged from 4.5 to 15.5 [55]. Other BSAF values for accumulation of PCB congeners from sediments by mayflies have been reported to range from 4.8 to 6.5 [56]. Biota–sediment accumulation factor values for accumulation of individual PCB congeners by the mussel (Malacoma nastu) ranged from 0.19 for PCB 209 to 4.74 for PCB 118 [54]. Those authors found a mean BSAF of 2.84 for all PCB congeners they examined. In a compilation of reported values [49], BSAF values range from 0.80 for the mayfly and 0.93 for the blue mussel (Mytilus edulis) to 5.11 for the bivalve mollusk (Yoldia limatula) and 5.30 for the midge (Chironomus spp.). The mean of median BSAF values for various species is 2.10 [49].

Few studies have measured BSAF values for the accumulation of organochlorines from sediments to trophic levels occupied by birds. One such study was conducted for PCBs as well as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans [57]. In that study, BSAF values ranging from 1.0 to 2.0 were measured for transfer from sediments to benthic invertebrates, and a range of BSAF values from less than 1.0 to approx. 10 were measured in diving ducks that eat benthic invertebrates. These values are similar to those observed in our study. In a study of the concentrations of total PCBs in the sediments and biota of western Lake Erie, a BSAF of 15 can be calculated for herring gull eggs from data presented by Koslowski et al. [58].

**Target sediment PCB concentrations**

Monitoring information can be used to predict concentrations of TEq in sediments that would be less than the threshold for adverse effects on birds. The sediment threshold concentration corresponding to the no-observable-adverse-effect level (NOAEL) in birds must first be calculated. Because no dose–response information is available for the effects of TEq on tree swallows, a consensus NOAEL for avian species of $7 \times 10^{-3}$ ng TEq/g wet weight in egg was used [23]. The average lipid content in the tree swallow eggs was 5.9%. Thus, the lipid-normalized NOAEL would be approx. $1.2 \times 10^{-1}$ ng TEq/g lipid. If the BSAF of 0.8 for tree swallow eggs (Table 5) is applied, the threshold concentration of TEq in sediments would be $1.5 \times 10^{-1}$ ng TEq/g TOC. The average concentration of TEq observed in sediments in this study was $1.1 \times 10^{-1}$ ng TEq/g TOC. This is a conservative value that would ensure safety for essentially all species and individuals. A value 10 to 20 times greater could be justified. This very conservative (protective) reference dose was used to calculate hazard quotients (HQs), defined as the ratio of the observed TEq in sediment to the calculated NOAEL TEq for sediment, in a one-tailed risk assessment. If the HQ calculated from this reference dose is less than 1.0, there would be little probability of observing any adverse effects in birds at the top of the sediment-based food chain. However, if the HQ were greater than 1.0, it would not mean that effects would be expected but that there was a level of concern such that a more refined risk assessment would be merited. Thus, the HQ would be approx. 0.7, which is less than the no-effect threshold HQ of 1.0. Thus, it is
unlikely that there would be adverse effects on birds feeding on insects emerging from these sediments.

SUMMARY

This study attempted to verify the use of BSAF ratios to predict concentrations of PCBs in tree swallow eggs and nestlings and to determine allowable concentrations of PCBs in sediments over which they were feeding that would be protective. The results of this study indicate that the patterns of relative concentrations of PCB congeners change with trophic level. If BSAF values are based on the sum of non- and mono-ortho-substituted PCB congeners or TEq, then the observed BSAF values are close to what would be predicted from fugacity theory. Thus, the concentrations of TEq measured in tissues of tree swallows might be used to predict an integrated measure of concentrations of TEq in sediments, and vice versa, by the application of a fairly simple partitioning model. A conservative (very protective) threshold concentration of TEq in sediments for adverse effects on birds was calculated to be $1.5 \times 10^{-1} \text{ ng TEq/g TOC}$. Based on this value and the BSAF determined for tree swallow nestlings, the HQ for sediments in this area was determined to be 0.7, which indicates that the dioxin-like activity of the PCB congeners in the sediments should not cause adverse effects on tree swallows at the locations studied in Saginaw Bay.

Acknowledgement—This study was supported under cooperative agreement GL995664 between the U.S. Environmental Protection Agency and Michigan State University and grant ES-04911 from the National Institutes of Health.

REFERENCES


**APPENDIX**

Toxic equivalency factors (TEFs) for mono-ortho and non-ortho polychlorinated biphenyls (PCBs) [33,34]

<table>
<thead>
<tr>
<th>PCB congener</th>
<th>TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>1.9E+03</td>
</tr>
<tr>
<td>77</td>
<td>1.8E+05</td>
</tr>
<tr>
<td>123</td>
<td>1.2E+05</td>
</tr>
<tr>
<td>118</td>
<td>3.5E+07</td>
</tr>
<tr>
<td>114</td>
<td>1.0E+07</td>
</tr>
<tr>
<td>105</td>
<td>8.0E-06</td>
</tr>
<tr>
<td>126</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>157</td>
<td>5.5E-05</td>
</tr>
<tr>
<td>156</td>
<td>1.5E-05</td>
</tr>
<tr>
<td>167</td>
<td>9.0E-06</td>
</tr>
<tr>
<td>169</td>
<td>4.7E-04</td>
</tr>
<tr>
<td>189</td>
<td>1.0E-05</td>
</tr>
</tbody>
</table>

* E = ×10^n.