*Environ. Sci. Technol.* **1998**, *32,* 1069−1075

# Aroclor 1268 and Toxaphene in Fish from a Southeastern U.S. Estuary

KEITH A. MARUYA* AND RICHARD F. LEE
*Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, Georgia 31411*

PCBs and toxaphene were analyzed in fish and their prey from an industrialized estuary in southeastern Georgia (USA). PCB concentrations were highest in forage fish (170 $\mu$g/g lipid) and were 1−3 orders of magnitude higher in biota from a heavily contaminated salt marsh in the upper estuary as compared with levels in similar species from two reference sites. Tissue PCB profiles matched that of Aroclor 1268, a highly chlorinated formulation used exclusively at a Superfund site in the upper estuary. Tissue profiles of fish gut contents and of species representing a simple food chain indicated that PCBs are likely transferred via the food web. Components of toxaphene, which was discharged from a facility in the lower estuary, were detected and confirmed in fatty organs of fish using gas chromatography with electron capture and mass spectrometric detection. Estimated toxaphene concentrations were 0.5−1 $\mu$g/g lipid. These results suggest that PCBs and toxaphene from point sources in different parts of the estuary are transferred locally through the food web and that fish transport these contaminants out of the heavily contaminated salt marshes during their semiannual movements within the estuary.

## Introduction

Polychlorinated biphenyls (PCBs) and components of technical toxaphene, also known as polychlorinated camphenes (PCCs), are ubiquitous hydrophobic organic contaminants that accumulate in biological tissues. This is particularly true for fish and fish-eating organisms that are long-lived and do not readily metabolize and/or quickly eliminate these contaminants (*1*−*7*). After adjusting for environmental concentrations, PCBs are in many cases thought to pose the greatest risk among chlorinated organic chemicals that exhibit "dioxin-like" biological activities (*8, 9*); the coplanar congeners (i.e., those with ≤2 *ortho*-chlorine substituents) are thought to be major contributors to potential toxicity (*10, 11*). Toxaphene, widely used as an agricultural pesticide before it was banned in the United States and other countries in the late 1980s, is acutely toxic to fish at low concentrations (∼1 $\mu$g/L) (*12*). Like PCBs and other halogenated organic compounds, there continues to be extensive research on the ecotoxicity of toxaphene (*13*).

Both PCBs and toxaphene were produced and used as technical mixtures; weight percentages of chlorine in PCB formulations ranged from 20% to 68% (*14*). Technical toxaphene consists of hundreds of individual bornane and bornene structures with 6−10 Cl atoms resulting in a mixture that is ∼70% chlorine (*15*). Because manufacturing processes were nonspecific, no individual component in PCB and toxaphene mixtures accounts for more than 15% of the total (*16*−*18*). In the environment, the difficulty encountered in comparing residues to source material and/or pure, unmodified standards is exacerbated by selective PCB/PCC transport, transformation, uptake, and accumulation processes (*19, 20*). Thus, the complexity of PCB/PCC profiles in contaminated aquatic biota makes it difficult to determine, with a high degree of confidence, sources, fates, effects, and the effectiveness of remediation strategies.

In an earlier paper, we documented the similarity of PCBs in heavily contaminated sediments from a salt marsh of the upper Turtle/Brunswick River Estuary in coastal Georgia (USA) to those found in Aroclor 1268 (*21*). The source of PCBs in this marsh was a former chlor-alkali plant that became a Superfund site in 1994. Although the potential for dioxin-like effects associated with sediment-associated Aroclor 1268 was estimated to be low relative to other, lesser chlorinated mixtures (*21*), the extent and congener distribution of PCB contamination in fish inhabiting this estuary has not been determined. In the lower estuary, discharge from a toxaphene manufacturer has contaminated sediments and resident biota in a salt marsh near Brunswick *(22*), several miles from the PCB-contaminated Superfund site. However, no data on toxaphene residues in estuarine biota of this system have been published since the early 1970s. In this work, we determined concentrations and congener profiles of PCBs and toxaphene in fish and their food sources from the upper and lower reaches of the estuary. Our objective was to assess the bioavailability and mobility of these sediment-associated contaminants, each originating from distinct point sources within the estuary.

## Materials and Methods

**Sample Collection.** Fish and crustaceans were collected using gill and dip nets from two locations in the Turtle/Brunswick River Estuary (Figure 1) during the spring of 1996. Specimens of spotted seatrout (*Cynoscion nebulosus*), red drum (*Sciaenops ocellatus*), striped mullet (*Mugil cephalus*), Southern flounder (*Paralichthys lethostigma*), and Atlantic croaker (*Micropogonias undulatus*) were collected near Dubignons Creek (DC) on the northwestern side of Jekyll Island in St. Simons Sound. Seatrout, yearling striped ("finger") mullet, and grass shrimp (*Paleomonetes pugio*) were collected near the discharge outfall of a former chlor-alkali facility (the LCP Chemicals Superfund site) in Purvis Creek (PC). Seatrout and red drum were taken from a third (reference) location, the Skidaway River (SR) near Savannah, GA, during the same time period. After collection, fish were measured, wrapped individually in clean aluminum foil, and placed in ice chests or directly into a freezer.

**Extraction and Cleanup Procedures.** Whole fish were defrosted and dissected on a glass cutting board using solvent-rinsed stainless steel instruments. Individual organs (including gonads, liver, and stomach/stomach contents) were removed, weighed, placed into precleaned I-Chem glass jars, and immediately frozen. Fillets of muscle were skinned and cut into small chunks. The cutting board and instruments were washed and rinsed with tap water and then with acetone prior to dissection of the next fish. All fish from the reference sites were dissected before fish from the contaminated site (Purvis Creek) to minimize cross-contamination.

Frozen tissues (5−30 g wet weight) were homogenized with an equal mass of kiln-fired $Na_2SO_4$ and extracted in a Soxhlet apparatus with 400 mL of $CH_2Cl_2$ for ≥16 h. Dibromooctafluorobiphenyl (DBOFB) was added to each

* Corresponding author telephone: 912-598-2306; fax: 912-598-2310; e-mail address: kam@skio.peachnet.edu.

S0013-936X(97)00809-2 CCC: $15.00 
Published on Web 03/06/1998

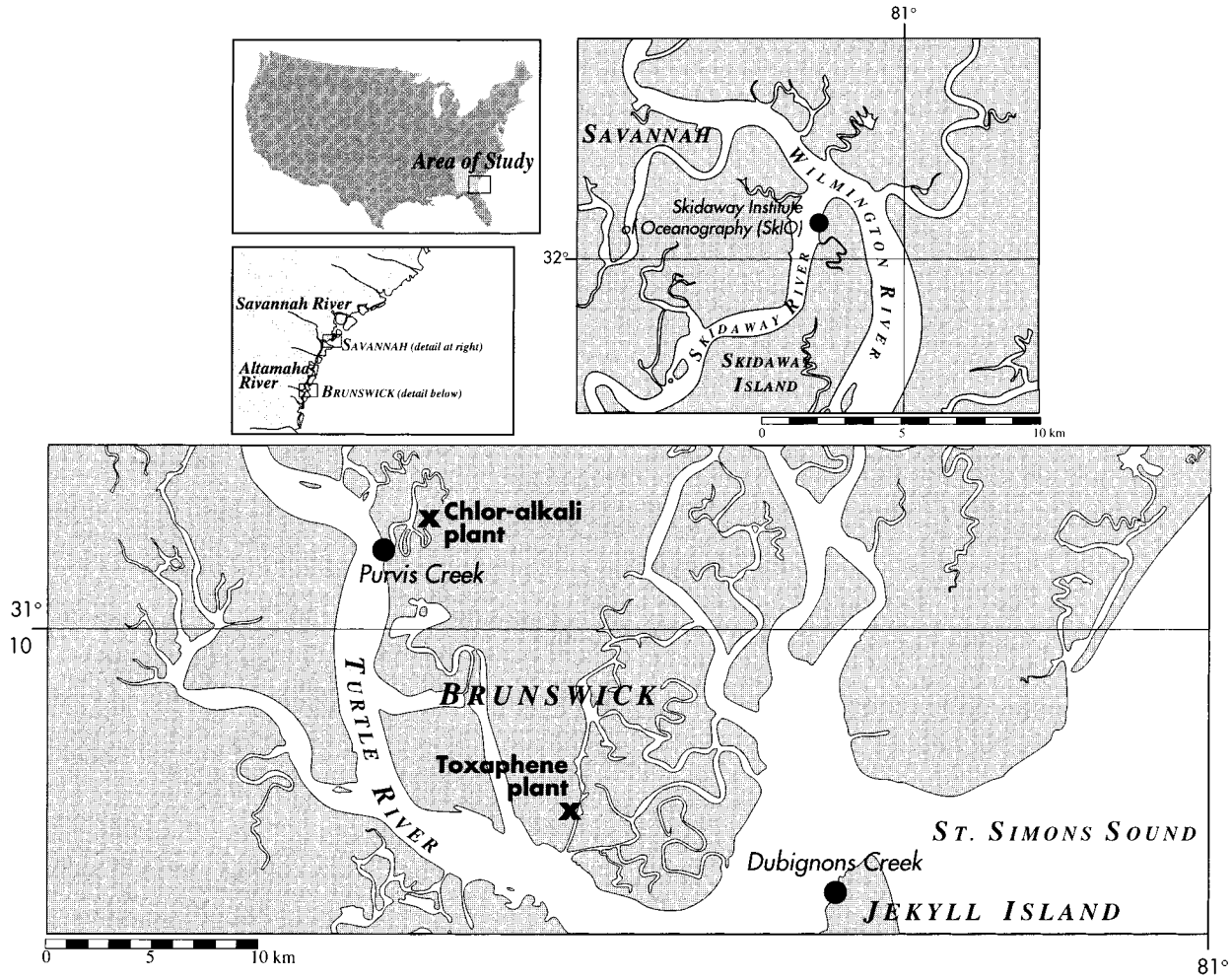


**FIGURE 1. Map of study area (coastal Georgia, USA) and sampling locations.**

sample as a recovery surrogate. $CH_2Cl_2$ extracts were reduced to ~10 mL in a Kuderna−Danish type concentrator. A small portion of this extract (20%) was set aside for gravimetric lipid determination. The remaining 80% of the Soxhlet extract was exchanged to hexane using a TurboVap II (Zymark; Hopkington, MA), reduced to ~2 mL and applied to a glass column packed with 18.0 g of 1.0% water (v/w) deactivated Florisil (60−100 mesh; Fisher Scientific, Fair Lawn, NJ). The Florisil had been previously activated at 550 °C in a muffle furnace for 24 h prior to deactivation. PCBs were eluted in 100−130 mL of hexane (fraction 1 or F1); toxaphene components and other organochlorine compounds were subsequently eluted with 150−200 mL of 50% $CH_2Cl_2$ in hexane (v/v; fraction 2 or F2)

**Instrumental Analysis.** Sample extracts were analyzed on a Varian 3400CX gas chromatograph with dual electron capture detection (GC−ECD) and on a similar GC coupled to a Saturn 3 ion trap mass spectrometer (ITMS) operating in the electron ionization (EI) mode. Fused silica columns (30 m × 0.25 mm i.d. × 0.25 $\mu$m film thickness; J&W Scientific, Folsom, CA) coated with DB-5 and DB-1701 were used for the dual-channel GC−ECD. A similar size column coated with DB-XLB was used for the ITMS. These instruments were calibrated with a 28-component PCB standard mixture (SRM2262; NIST, Gaithersburg, MD, USA), a toxaphene standard (Ultra Scientific, North Kingstown, RI), and individual hepta-, octa-, and nonachlorobiphenyl congeners (Ultra Scientific or AccuStandard, New Haven, CT). Full scan mass spectra (50−650 Da at 1 scan/s) and DB-5/DB-XLB retention times were recorded and catalogued for each PCB congener in SRM2262 and for all individual congeners with ≥7 chlorine atoms (i.e., IUPAC Nos. 169−209).

The confirmation of toxaphene components was performed using GC−negative chemical ionization MS (GC−NCIMS). Methane and helium were the chemical ionization and carrier gases, respectively. Selected extracts were concentrated to 50−500 $\mu$L and analyzed using a Hewlett-Packard 5890 Series II GC with a 30 m × 0.1 $\mu$m film thickness DB-5 column (J&W Scientific) coupled to a Finnigan INCOS 50 quadrupole mass spectrometer operating in the scanning mode (250−450 Da at 0.6 scans/s). The GC column oven was programmed between 100 and 300 °C at 5 °C/min. Concentrations of total toxaphene were estimated from the summed response of the 20 largest peaks eluting in a 15−20 min time window for standard injections of 510 and 1020 pg for each GC−ECD channel. The summed areas of the same 20 peaks in tissue GC−ECD chromatograms were then divided by the total toxaphene response factor. In this manner, total toxaphene was computed independently for each column (i.e., DB-5 and DB-1701). Suspected toxaphene peaks eluting at retention times coinciding with other organochlorine pesticides (±0.05 s) were not included in these estimates.

**Quality Assurance Provisions.** The method detection limits (MDLs) for the ECD-based procedure were ~0.06 and ~10 ng/g for individual PCBs and total toxaphene, respectively, based on a 20 g wet tissue sample. Check standards (SRM2262 and difluorotriphenylphosphine) were injected periodically to monitor instrument drift and mass calibration of the GC−ITMS. The mean recovery of DBOFB in F1 extracts

**TABLE 1. Lipid Content and ΣPCBs in Fish Tissues and Whole Grass Shrimp (mean ± SD)**

| location/species | tissue type | *n* | estd age (yr) | % lipid | ΣPCBs (μg/g) wet wt | ΣPCBs (μg/g) lipid wt |
|---|---|---|---|---|---|---|
| | | | **Purvis Creek (PC)** | | | |
| spotted seatrout | | 3 | 2−4 | | | |
| | muscle | 3 | | 1.2 ± 0.65 | 0.48 ± 0.24 | 44 ± 7.2 |
| | ova | 3 | | 6.6 ± 1.6 | 1.9 ± 0.41 | 31 ± 12 |
| | liver | 3 | | 8.4 ± 1.2 | 3.0 ± 1.2 | 34 ± 11 |
| | gut contents | 1 | | 0.31 | 0.27 | 87 |
| striped mullet | whole body | 4 | <1 | 0.46 ± 0.065 | 0.78 ± 0.21 | 170 ± 34 |
| grass shrimp | whole | 3 | na[a] | 1.7 ± 0.43 | 0.33 ± 0.068 | 20 ± 2.4 |
| | | | **Dubignons Creek (DC)** | | | |
| spotted seatrout | | 1 | 3 | | | |
| | muscle | 1 | | 0.54 | 0.036 | 6.6 |
| | ova | 1 | | 7.2 | 0.41 | 5.7 |
| red drum | | 1 | 0.8 | | | |
| | muscle | 1 | | 0.12 | 0.0076 | 6.3 |
| | liver | 1 | | 4.1 | 0.54 | 13 |
| | gut contents | 1 | | 0.37 | 0.027 | 7.3 |
| striped mullet | | 1 | na | | | |
| | muscle | 1 | | 0.24 | 0.0070 | 2.9 |
| Atlantic croaker | | 1 | 2 | | | |
| | muscle | 1 | | 0.51 | 0.015 | 2.9 |
| | ova | 1 | | 10 | 0.39 | 3.7 |
| | | | **Skidaway River (SR)** | | | |
| spotted seatrout | | 3 | 1−3 | | | |
| | muscle | 3 | | 0.84 ± 0.19 | 0.0062 ± 0.00090 | 0.76 ± 0.074 |
| | ova | 1 | | 1.4 | 0.0051 | 0.36 |
| red drum | | 1 | 1 | | | |
| | muscle | 1 | | 0.24 | 0.0025 | 1.1 |

[a] na, not available.

was 94 ± 7.8%. The analysis of fish muscle spiked with 20 PCB congeners (mono- to decachlorobiphenyl) and of CARP-1 (NRCC, Ottawa, Canada) using these procedures resulted in mean recoveries of 90 ± 6.5% and 102 ± 12% for spiked and native congeners, respectively. Procedural blanks consisting of 40−50 g of kiln-fired $Na_2SO_4$ did not contain target PCBs at ≥3 times the nominal MDL and gave no indication of toxaphene or other organochlorine pesticide contamination.

The presence of individual PCB congeners whose concentrations were >0.5 ng/g wet wt was confirmed by GC−ITMS. The DB-XLB stationary phase is similar in polarity to DB-5 but was able to resolve many of the congeners that typically coelute using the latter stationary phase. Thus, IUPAC Nos. 66, 153, 132, 105, 138, 163/164, 187, 182, 159, 170, and 190 were resolvable by GC−ITMS. The elution order of the higher chlorinated congeners (i.e., 179, 183, 185, 174, 202, 200, 199, 196, 208, and 207) matched that of others without exception (*23, 24*).

## Results

**PCB Concentrations and Congener Profiles.** Total PCB concentrations as the sum of 43 congeners are summarized for tissues in Table 1. Individual fish age was estimated from length−weight−age correlations (*25*). Total PCBs in muscle were lowest in reference (SR) seatrout (~5 ng/g wet wt) and highest in upper estuary (PC) seatrout (~500 ng/g) with concentrations in lower estuary (DC) fish being intermediate between the two extremes. Compared with muscle, total PCBs in fatty tissues (i.e., liver and ova) was an order of magnitude or more higher. On a wet weight basis, the highest PCB concentrations were measured in liver and ova of mature seatrout from Purvis Creek. On a lipid basis, PCBs were highest in Purvis Creek finger mullet (170 μg/g). The qualitative nature of the prominent peaks in GC−ITMS total ion chromatograms was similar among F1 tissue extracts of biota from both Turtle/Brunswick stations (Figure 2). Chromatograms of our Aroclor 1268 standard and Purvis Creek marsh sediment, the only known source of Aroclor 1268 in this estuary, are also included for comparison. Note the enrichment of earlier eluting PCBs (peak numbers 2−10 in Figure 2) relative to IUPAC Nos. 206 and 209 (peak numbers 14 and 15) in tissue extracts relative to sediment and Aroclor 1268. The profile in Purvis Creek finger mullet more closely resembled that of Aroclor 1268 than the other tissues. F1 chromatograms of Skidaway River tissues (not shown) did not exhibit this general pattern of late eluting, highly chlorinated PCBs.

Twelve congeners—IUPAC Nos. 187, 202, 201, 180, 200, 199, 196, 208, 207, 194, 206, and 209—accounted for >90% of the total PCB concentrations in Purvis Creek grass shrimp, mullet, and seatrout, animals representing three levels of the local food web. A comparison of the relative abundance rankings of these congeners in these animals indicated a progressive decrease in 9- and 10-Cl PCBs and concomitant

**TABLE 2. Rankings of the 12 Most Abundant PCB Congeners in Tissue and Sediment from Purvis Creek**

| IUPAC No. | no. of Cl atoms | log $K_{ow}$[a] | Aroclor 1268 | marsh sediment | grass shrimp | striped mullet | seatrout ova |
|---|---|---|---|---|---|---|---|
| 187[b] | 7 | 7.18 | 8 | 6 | 4 | 6 | 5 |
| 199[b] | 8 | 7.21 | 2 | 2 | 1 | 2 | 1 |
| 200 | 8 | 7.28 | 12 | 12 | 12 | 12 | 12 |
| 180[b] | 7 | 7.37 | 11 | 10 | 9 | 11 | 9 |
| 201[b] | 8 | 7.63 | 10 | 11 | 10 | 10 | 8 |
| 196[b] | 8 | 7.66 | 4 | 4 | 3 | 4 | 2 |
| 207[c] | 9 | 7.75 | 9 | 9 | 11 | 9 | 10 |
| 208[c] | 9 | 8.16 | 3 | 3 | 6 | 3 | 6 |
| 202 | 8 | 8.42 | 5 | 5 | 5 | 5 | 4 |
| 194 | 8 | 8.68 | 7 | 8 | 7 | 7 | 7 |
| 206[c] | 9 | 9.14 | 1 | 1 | 2 | 1 | 3 |
| 209[c] | 10 | 9.60 | 6 | 7 | 8 | 8 | 11 |

[a] From Eisler and Belisle (*26*). [b] Increased in abundance in tissues. [c] Decreased in abundance in tissues.

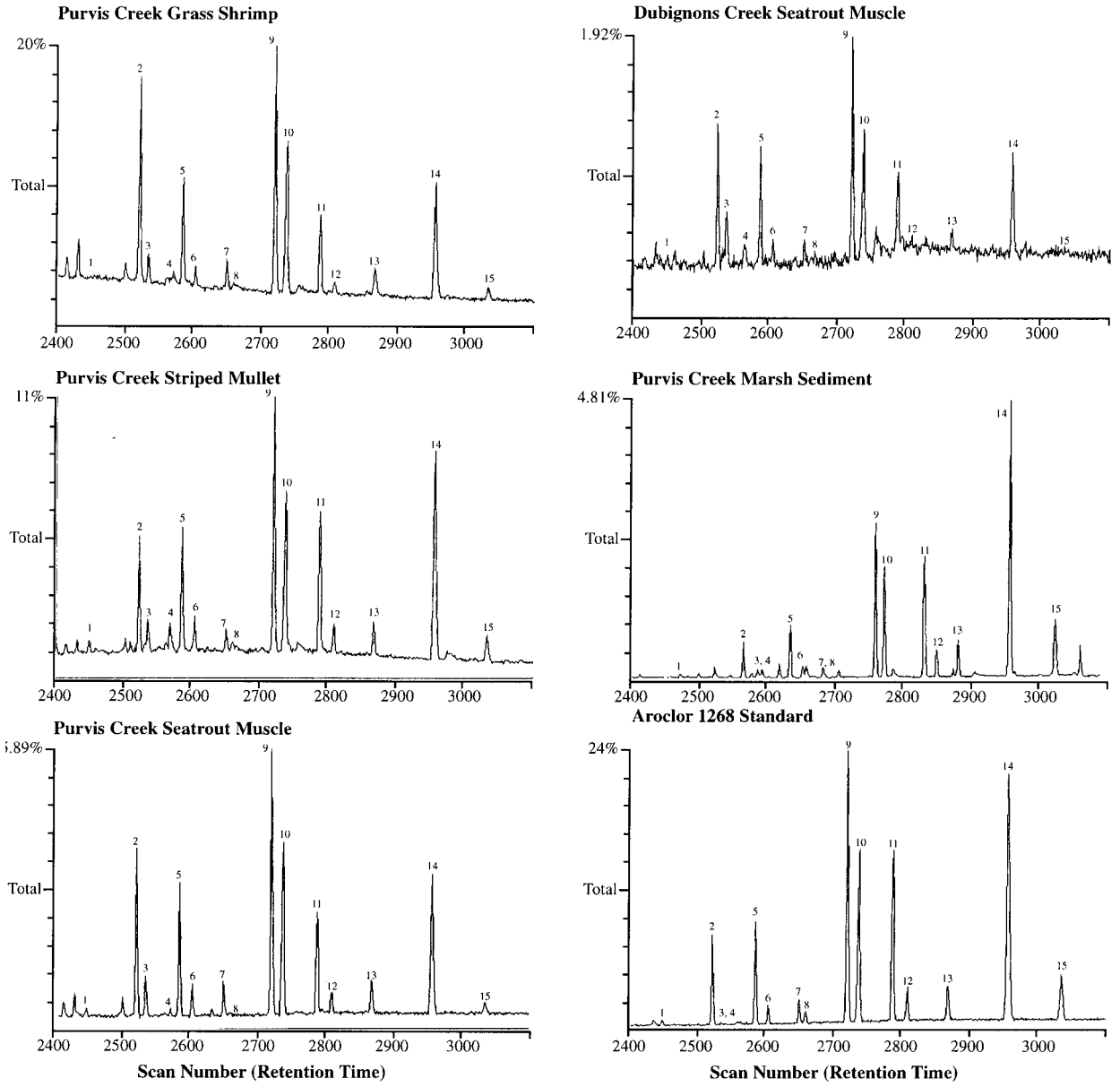


**FIGURE 2. GC−MS total ion chromatograms of Purvis Creek grass shrimp, striped mullet, and spotted seatrout muscle; Dubignons Creek seatrout muscle; Purvis Creek marsh sediment; and an Aroclor 1268 standard. Peak and corresponding IUPAC numbers: 1 = 179; 2 = 187; 3 = 183; 4 = 185; 5 = 202; 6 = 201; 7 = 180; 8 = 200; 9 = 199; 10 = 196; 11 = 208; 12 = 207; 13 = 194; 14 = 206; 15 = 209.**

increase in 7-Cl PCBs (Table 2). The relative abundances of these congeners in gut contents, muscle, liver, and ova of a 4-year-old seatrout from Purvis Creek were very similar, with a slight decreasing abundance of IUPAC Nos. 206 and 209 from gut contents to fatty organs (Figure 3). Homologue distributions in Skidaway River tissues were dominated by congeners with 3−7 chlorines (not shown); none of the characteristic Aroclor 1268 congeners were detected.

**Confirmation of Toxaphene and Estimated Total Concentrations.** GC−NCIMS analysis of selected F2 extracts, including those of Purvis Creek seatrout liver and Dubignons Creek croaker ova, confirmed the presence of hexa-, hepta-, and octachlorinated toxaphene components (Figure 4). A complex series of peaks in GC−ECD chromatograms was observed in these and several other F2 extracts, many of which corresponded with prominent peaks in our toxaphene standard (Figure 5). Estimated toxaphene concentrations for samples in which ≥10 of the 20 most abundant peaks in our toxaphene standard were present, omitting peaks that coeluted with other organochlorines, ranged between 20 and 130 ng/g wet wt (480−1040 ng/g lipid) (Table 3). No such GC−ECD pattern was observed in Purvis Creek grass shrimp or finger mullet or in fish from the Skidaway River.

## Discussion

**PCB and Toxaphene Concentrations.** Tissue PCB concentrations reported herein are comparable with previously published data for various species of fish and aquatic invertebrates from impacted areas. Total PCBs in muscle and in whole fish in this study were similar to those reported for white croaker from southern California waters (*27*), striped mullet from Japan, and winter flounder from Long Island Sound, NY (*26*). In contrast, PCBs in this study were less than that found in Great Lakes salmonids and striped bass from Long Island Sound. PCBs in Purvis Creek seatrout eggs were one-third of the levels found in eggs of Lake Michigan chinook salmon (*28*), similar to levels in lake trout eggs from other Great Lakes locations (*29*), and much higher than concentrations in Atlantic salmon ova from the Baltic Sea (*26*). Total PCBs in fish liver from this study were similar to

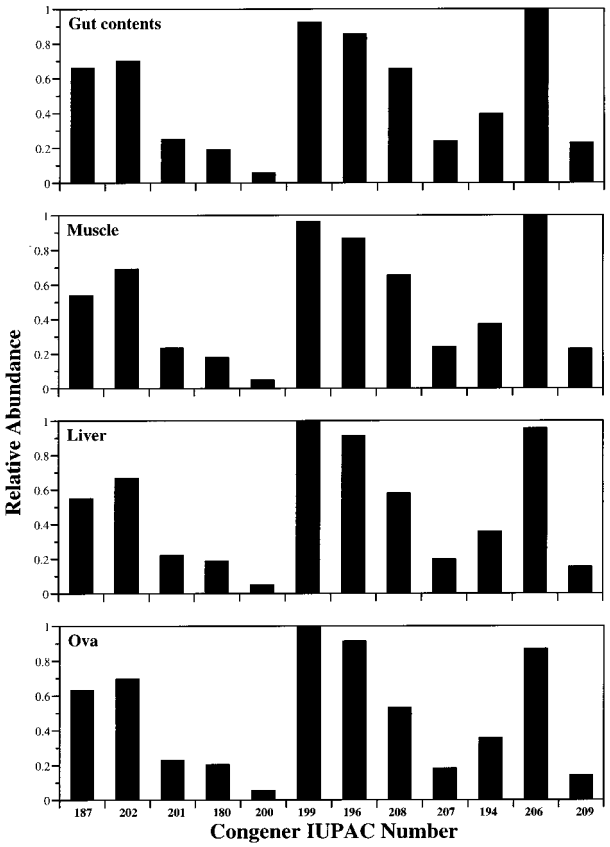


**FIGURE 3. Relative distribution of the 12 most abundant PCB congeners in gut contents, muscle, liver, and ova of a seatrout from Purvis Creek.**

those found in New Jersey tilefish and Long Island Sound winter flounder, but were much less than levels in winter flounder from New Bedford Harbor, MA (*26*). Total PCBs in grass shrimp in this study were much less than that reported for the same species (*P. pugio*) from New Bedford Harbor (*30*) but were similar to that found in the hepatopancreas of blue crab from the Elizabeth River Estuary in Virginia (*31*).

Estimated toxaphene concentrations in ova and liver in our study were similar to those reported in 2-year-old rainbow trout from two toxaphene-treated lakes in Alberta, Canada (*32*), and were up to 10 times higher than that reported for muscle and liver of Canadian and North Atlantic cod species (*2, 12*). Our estimates were an order of magnitude lower than toxaphene levels reported in freshwater burbot liver from the Canadian arctic (*33*) and that for lake trout from the Great Lakes (*20*). In this latter study, both lipid and wet weight toxaphene concentrations in smaller, presumably younger fish (e.g., smelt) were similar to the levels found in the present study. Our liver and ova wet weight concentrations were several orders of magnitude less than that reported more than 2 decades ago for penaeid shrimp and small, nonmigratory fish (*Fundulus* sp.) from the toxaphene-contaminated marsh near Brunswick, GA (*22*).

**PCB Congener and Toxaphene Profiles.** The distribution and predominance of congeners with ≥7 chlorines including IUPAC Nos. 174, 183, 199, 196, 206, 207, and 208) clearly indicated the accumulation of congeners prevalent in Aroclor 1268 (*21*) in biota from Purvis and Dubignons Creeks. These profiles were in contrast to the distribution in Skidaway River fish and also with those reported in other surveys. The predominant homologues in these cases were tri- through hepta PCBs, and the predominant congeners were typically IUPAC Nos. 44, 52, 66, 87, 95, 101, 110, 105, 118, 128, 138, 153, 170, and 180 (this study, *27, 34, 35*), indicating that PCBs

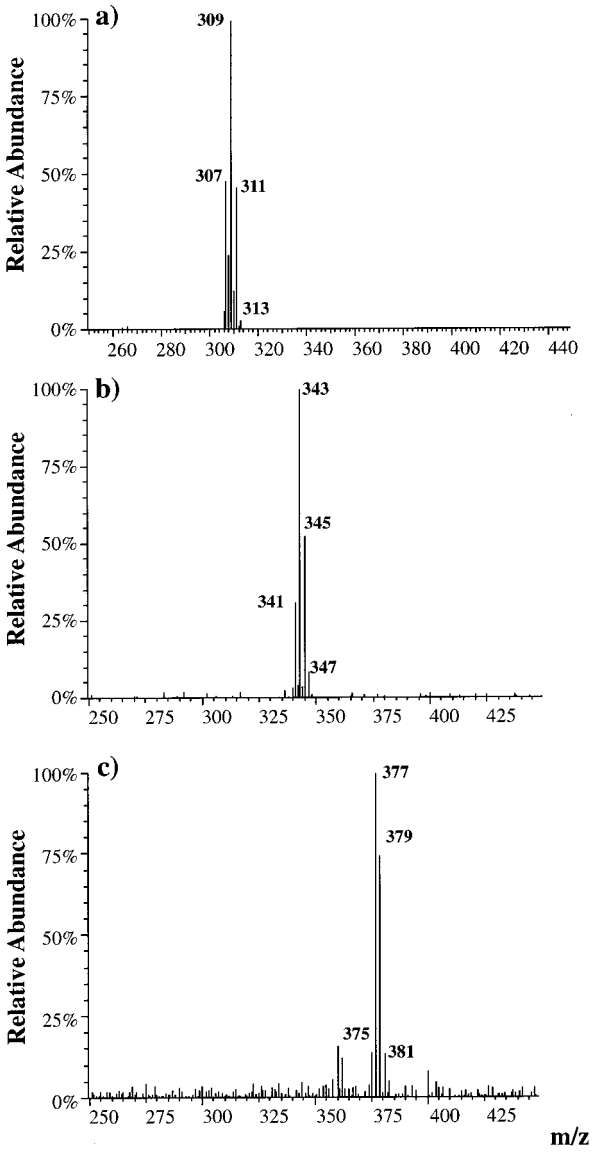


**FIGURE 4. Mass spectra of prominent (a) hexa- (*m/z* 307−313); (b) hepta- (*m/z* 341−347); and (c) octachlorinated (*m/z* 375−381) toxaphene homologues in the fraction 2 liver extract of a seatrout from Purvis Creek.**

found in SR fish originated from more commonly used, lesser chlorinated PCB mixtures. It is possible that the hepta- and octachlorinated congeners IUPAC Nos. 174, 183, 187, 194, and 196 in tissues of this study could have resulted from Aroclor 1260; however, the relatively low abundance of other prominent Aroclor 1260 components (e.g., IUPAC Nos. 138, 149, 153, and 170) suggest that this mixture is a minor contributor of PCBs in these tissues.

The distribution of PCBs in samples from Purvis Creek was shifted in favor of lower chlorinated Aroclor 1268 congeners as compared to marsh sediment (Table 2), the source of accumulated PCBs (this study, *21*). In related work, the authors found a negative correlation between biota sediment accumulation factors (BSAFs) and $K_{ow}$ (*36*). Moreover, the pattern of chlorine substitution appeared to influence bioaccumulation within a homologous series. In New Bedford Harbor, the selective bioaccumulation of certain congeners in grass shrimp and small forage fish were attributed to metabolic processes (*30*). The metabolism of Aroclor 1268 congeners, which average 8.5 chlorines per biphenyl (*21*), by fish in this study seems unlikely. A more likely scenario was the selective uptake and bioaccumulation

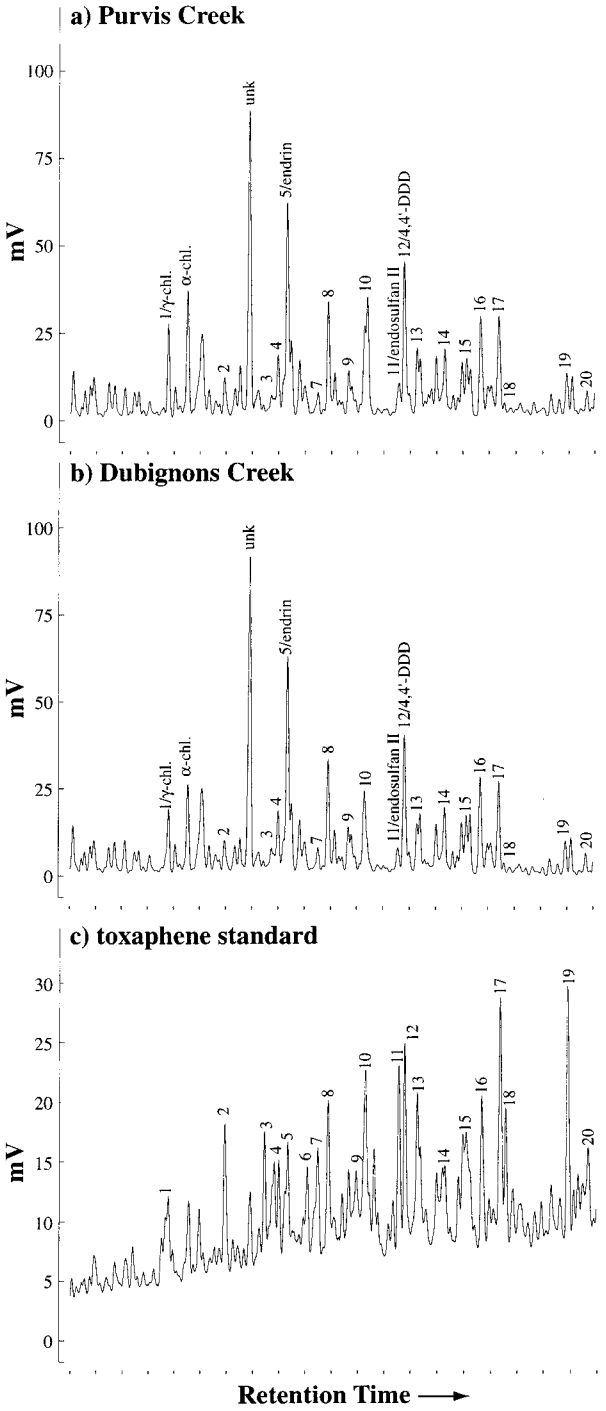


**FIGURE 5. GC−ECD chromatograms (DB-1701) of seatrout ova from the (a) upper and (b) lower Turtle/Brunswick River estuary and (c) of a toxaphene standard. Peak numbers correspond to the 20 most abundant components in © that were used to estimate total toxaphene concentrations. (chl. = chlordane; unk = unknown).**

of congeners according to (i) their hydrophobicity (i.e., $K_{ow}$) and (ii) chlorine substitution patterns (e.g., enhanced for di-*ortho*-substituted congeners IUPAC Nos. 180 and 194; decreased for the fully *ortho*-substituted congener IUPAC No. 200) (*36*). An exception to decreasing bioaccumulation with increasing hydrophobicity was noted for Purvis Creek mullet, which exhibited a pattern that more closely mimicked unmodified Aroclor 1268 and marsh sediment. This is not surprising as the young of this species are known to ingest surface sediment that contains preferred food items (benthic algae, microcrustaceans) (*37, 38*).

**TABLE 3. Estimated Concentrations of Total Toxaphene (Mean ± SD)[a]**

| location/species | tissue type | Σtoxaphene (ng/g lipid wt) | Σtoxaphene (ng/g wet wt) |
|---|---|---|---|
| **Dubignons Creek** | | | |
| spotted seatrout | ova | 56 ± 5.6 | 780 ± 77 |
| Atlantic croaker | ova | 69 ± 17 | 660 ± 160 |
| southern flounder | liver | 130 ± 8.7 | 540 ± 36 |
| red drum | liver | 20 ± 0.22 | 480 ± 5.4 |
| **Purvis Creek** | | | |
| spotted seatrout no. 1 | liver | 60 ± 12 | 780 ± 160 |
| | ova | 46 ± 0.22 | 1040 ± 5.0 |
| spotted seatrout no. 2 | liver | 39 ± 16 | 520 ± 210 |
| | ova | 51 ± 5.1 | 610 ± 61 |
| spotted seatrout no. 3 | liver | 66 ± 15 | 660 ± 150 |
| striped finger mullet | whole body | <10 | <2500 |
| grass shrimp | whole | <10 | <1500 |
| **Skidaway River** | | | |
| spotted seatrout | ova | <10 | < 700 |

[a] Averaged from the results of the dual-column GC−ECD analysis.

A relatively small number of hexa-, hepta-, and octachlorinated PCCs were confirmed by GC−NCIMS in fish liver and ova samples. However, our dual-column GC−ECD analysis indicated the likely presence of additional toxaphene components. Toxaphene homologue distributions in fish have previously been reported to be simple in some cases, consisting of only a few congeners (*12, 33*). In other instances, the toxaphene pattern was complex, with the degree of chlorination varying substantially (*20*). More work is needed to further characterize the PCC distribution in these and other samples from this estuary.

**Utility of Aroclor 1268 and Toxaphene Monitoring in Future Studies**. PCB concentrations were orders of magnitude greater in fish from the Turtle/Brunswick River Estuary as compared with similar species from the Skidaway River, a reference site along the Georgia coast. The highly chlorinated components of Aroclor 1268 dominated the PCB profile in predator fish, including those from a station 25−30 km from the source of PCB contamination. A similar profile in prey species and predator fish gut contents suggests that contaminated food is an important source of these extremely hydrophobic PCBs (log $K_{ow}$ range: 6.5−9). Similarly, toxaphene was found to be elevated in fatty organs of predator fish from the upper and lower Turtle/Brunswick River Estuary. No evidence of toxaphene residues was found in resident, nonmigratory prey items (grass shrimp, finger mullet) from Purvis Creek, which is several kilometers from the area of heavy toxaphene contamination.

These results indicate that Aroclor 1268 PCBs and toxaphene are available to prey and predator fish and accumulate preferentially in fatty organs. PCBs (and perhaps toxaphene) are likely taken up by resident prey animals in heavily contaminated marshes, which are in turn consumed by larger fish during their seasonal movements throughout the estuary. As they continue their semiannual movements, contaminated predator fish and other mobile species such as blue crab and penaeid shrimp act as contaminant "vectors", transporting otherwise strongly sorbing hydrophobic contaminants to different parts of the estuary where they may be harvested and consumed by higher predators (e.g., marine mammals, humans).

Because of their unique congener compositions, point source characteristics, environmental recalcitrance, and bioaccumulation/biotransfer potential, even after decades of environmental exposure, the determination of concentrations and congener distributions of Aroclor 1268 and toxaphene in water, sediment, and biota from this estuary will

be useful in expanding our limited knowledge of the behavior of these extremely hydrophobic organic contaminants. Longer term studies that include monitoring of these contaminants would also assist in evaluating the effectiveness of current and future remediation and mitigation efforts planned for the contaminated salt marshes of this estuary.

## Acknowledgments

The authors gratefully acknowledge the efforts of S. Wakeham, S. McCumber-Kahn, and A. Boyette of the Skidaway Institute of Oceanography; P. Peronard and L. Francendese of the EPA; and F. Nicholson of the Georgia Department of Natural Resources. This study was funded in part by the National Science Foundation (DEB-9706317).

## Literature Cited

(1) Delany, M. F.; Bell, J. U.; Sundlof, S. F. *J. Wildl. Dis.* **1988**, *24*, 562−566.
(2) Muir, D. C. G.; Norstrom, R. J.; Simon, M. *Environ. Sci. Technol.* **1988**, *22*, 1071−1079.
(3) Tanabe, S.; Subramanian, A.; Ramesh, A.; Kumaran, P. L.; Miyazaki, N.; Tatsukawa, R. *Mar. Pollut. Bull.* **1993**, *26*, 311−316.
(4) Voldner, E. C. *Chemosphere* **1993**, *27*, 2073−2078.
(5) Elskus, A. A.; Stegeman, J. J.; Gooch, J. W.; Black, D. E.; Pruell, R. J. *Environ. Sci. Technol.* **1994**, *28*, 401−407.
(6) Falandysz, J.; Yamashita, N.; Tanabe, S.; Tatsukawa, R.; Rucinska, L.; Mizera, T.; Jakuczun, B. *Arch. Environ. Contam. Toxicol.* **1994**, *26*, 13−22.
(7) Hong, C. S.; Xiao, J.; Casey, A. C.; Bush, B.; Fitzgerald, E. F.; Hwang, S. A. *Arch. Environ. Contam. Toxicol.* **1994**, *27*, 431−437.
(8) Steinwandter, H. *Fresenius J. Anal. Chem.* **1992**, *342*, 416−420.
(9) Giesy, J. P., et al. *Arch. Environ. Contam. Toxicol.* **1994**, *27*, 213−223.
(10) Safe, S. *Crit. Rev. Toxicol.* **1984**, *13*, 319−393.
(11) Kannan, N.; Tanabe, S.; Ono, N.; Tatsukawa, R. *Arch. Environ. Contam. Toxicol.* **1989**, *18*, 850−857.
(12) Oehme, M.; Schlabach, M.; Kallenborn, R.; Haugen, J. E. *Sci. Total Environ.* **1996**, *186*, 13−24.
(13) Lockhart, W. L., et al. *Chemosphere* **1993**, *27*, 1841−1848.
(14) Hutzinger, O.; Safe, S.; Zitko, V. *The Chemistry of PCBs*; Krieger Publishing: Malabar, FL, 1983.
(15) Saleh, M. A. In *Reviews of Environmental Contamination and Toxicology, Vol. 118;* Ware, G. W., Ed.; Springer-Verlag: New York, 1991; pp 1−85.
(16) Schulz, D. E.; Petrick, G.; Duinker, J. C. *Environ. Sci. Technol.* **1989**, *23*, 852−859.
(17) Zhu, J.; Mulvihill, M. J.; Norstrom, R. J. *J. Chromatogr. A* **1994**, *669*, 103−117.
(18) Alder, L.; Vieth, B. *Fresenius J. Anal. Chem.* **1996**, *354*, 81−92.
(19) Eisler, R. *Polychlorinated Biphenyl Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review;* Biological Report 85(1.7); U.S. Department of Interior, Fish and Wildlife Service: Laurel, MD, 1986.
(20) Glassmeyer, S. T.; DeVault, D. S.; Meyers, T. R.; Hites, R. A. *Environ. Sci. Technol.* **1997**, *31*, 84−88.
(21) Kannan, K.; Maruya, K. A.; Tanabe, S. *Environ. Sci. Technol.* **1997**, *31*, 1483−1488.
(22) Reimhold, R. J.; Durant, C. J. *Pestici. Monit. J.* **1974**, *8*, 44−49.
(23) Frame, G. M.; Cochran, J. W.; Bowadt, S. S. *J. High-Resolut. Chromatogr.* **1996**, *19*, 657−668.
(24) J&W Scientific. *Congener Specific PCB Analysis with DB-XLB by GC−MS*; Environmental Application Note E10; J&W Scientific, Inc.: Folsom, CA, 1996.
(25) Music, J. L., Jr.; Pafford, J. M. *Population Dynamics and Life History Aspects of Major Marine Sportfishes in Georgia's Coastal Waters*; Contribution Series 38; Georgia Department of Natural Resources: Brunswick, GA, 1984.
(26) Eisler, R.; Belisle, A. A. *Planar PCB Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review*; Biological Report 31; U.S. Department of Interior, National Biological Service: Washington, DC, 1996.
(27) Draper, W. M.; Koszdin, S. *J. Agric. Food Chem.* **1991**, *39*, 1457−1467.
(28) Williams, L. L.; Giesy, J. P. *J. Great Lakes Res.* **1992**, *18*, 108−124.
(29) Mac, M. J.; Schwartz, T. R.; Edsall, C. C.; Frank, A. M. *J. Great Lakes Res.* **1993**, *19*, 752−765.
(30) Lake J. L.; McKinney, R.; Lake, C. A.; Osterman, F. A.; Heltshe, J. *Arch. Environ. Contam. Toxicol.* **1995**, *29*, 207−220.
(31) Mothershead, R. F., II; Hale, R. C.; Greaves, J. *Environ. Toxicol. Chem.* **1991**, *10*, 1341−1349.
(32) Miskimmin, B. M.; Muir, D. C. G.; Schindler, D. W.; Stern, G. A.; Grift, N. P. *Environ. Sci. Technol.* **1995**, *29*, 2490−2495.
(33) Bidleman, T. F.; Walla, M. D.; Muir, D. C. G.; Stern, G. A. *Environ. Toxicol. Chem.* **1993**, *12*, 701−709.
(34) Niimi, A. J.; Oliver, B. G. *Environ. Sci. Technol.* **1989**, *23*, 83−88.
(35) Maack, L.; Sonzogni, W. C. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 711−719.
(36) Maruya, K. A.; Lee, R. F. *Environ. Toxicol. Chem.* In press.
(37) Odum, W. E. In *Marine Food Chains*; Steele, J. J., Ed.; Oliver and Boyd, Ltd: Edinburgh, Scotland, 1974; pp 222−240.
(38) Collins, M. R. *J. Fish Biol.* **1981**, *19*, 307−315.

*Received for review September 9, 1997. Revised manuscript received January 26, 1998. Accepted January 30, 1998.*

ES970809K