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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MARCH 2004

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Spatial Variation in Hepatic Levels and Patterns of PCBs and PCDD/Fs among Young-of-the-Year and Adult Atlantic Tomcod (*Microgadus tomcod)* in the Hudson River Estuary

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Full congener-specific polychorinated biphenyl (PCB) and partial-congener-specific polychorinated dibenzo-*p*-dioxin/furan (PCDD/F) analyses were performed on livers from young-of-the-year (YOY) and adult Atlantic tomcod from the Hudson River estuary including multiple sites along the main-stem Hudson River and Newark Bay/Hackensack River, NJ, and from a reference river, the Miramichi River, NB. Highest hepatic burdens of PCBs were found in fish collected in the main-stem Hudson River between river miles (RM) 37 and 50 and in Newark Bay/Hackensack River. By far, the highest concentrations of PCDD/Fs were seen in fish from Newark Bay/Hackensack River. The di- to tetrachlorinated biphenyls dominated the PCB composition in YOY tomcod, whereas the penta- to nonachlorinated biphenyls predominated in adults with particular prevalence of the 2,4,5-substituted diortho congeners. Overall, using a direct mixing model an aroclor composition of approximate 1:1:1, A1242:A1254:A1260, was calculated from the hepatic PCB profiles in YOY tomcod. A linear increase in A1242 characteristics with river mile was seen in YOY collected between RM 0 and RM 80, which was likely due to the well-characterized A1242 source from the former capacitor manufacturing plants located upriver. However, tomcod caught upstream of RM 80 exhibited a PCB pattern with decreasing A1242 characteristics, and it was hypothesized that this was due to the increased depuration or decreased uptake of low chlorinated (log $K_{OW} < 6$) congeners upon entry of the fish into freshwater from brackish water. The most abundant tetra−octa PCDD/F chlorohomologue in tomcod collected from the main stem of the Hudson River was TCDF, whereas 2,3,7,8-TCDD was the major congener detected in tomcod from Newark Bay/Hackensack River, which showed elevated total PCDD/F levels compared to tomcod from the main-stem Hudson River.

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Introduction

Polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) bioaccumulate and often biomagnify in food chains. Certain congeners exhibit toxicities similar to that of highly toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) including dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine function (*1, 2*). Furthermore, hydroxylated PCBs and PCDD/Fs have been found to disrupt thyroid function by binding to thyroid transport proteins in higher animals (*3, 4*). The Stockholm Convention, a global treaty aimed at eliminating 12 of the most widespread and toxic persistent organic pollutants (POPs), was signed by 151 nations between May 2001 and May 2002, including Canada and the United States. Once ratified, the treaty calls for the elimination of nine intentionally produced and used chemicals, including PCBs, and for strong action to prevent or reduce unintentional production of PCDD/Fs, PCBs, and hexachlorobenzene (HCB) (*5*). Nevertheless, PCBs and PCDD/Fs are highly persistent with environmental half-lives often decadal in scale and may still account for the majority of "dioxin-like" toxic effects elicited in organisms in aquatic environments.

One highly impacted ecosystem is the Hudson River, New York (NY) and New Jersey (NJ), where the lower 200 mi. have been designated a U.S. Federal Superfund site by the U.S. Environmental Protection Agency (USEPA) since 1983. An estimated 95 000−603 000 kg of PCBs was discharged from the late 1940s to 1977 from two General Electric capacitor manufacturing plants located at river miles (RM) 196 and 197 at Fort Edward, NY, and Hudson Falls, NY, respectively (*6*). More recently, PCB flux to the lower Hudson River estuary originates from the riverbed between Hudson Falls and New York which acted as the primary sink for aroclors 1242 and 1016 (i.e., from General Electric plants) and from wastewater effluents discharged into the lower Hudson River estuary which exhibit primarily an aroclor 1254 and 1260 pattern (*7, 8*).

Numerous reports document high body burdens of total PCBs (tPCBs) and, in some cases, homologue and/or congener patterns in Hudson River resource species, usually targeting striped bass (*Morone saxatilis*) and occasionally other ecologically important species (*9*−*12*). However, with very few exceptions (*13*; Steinbacher and Baker, unpublished data) there is very little congener-specific data for PCBs in Hudson River species. Similarly, only a few studies (*14, 15*) have investigated the toxicological effects of PCB contamination on the biota of the Hudson River ecosystem. Many, although not all, toxicities of PCBs and PCDD/Fs in vertebrates, including fish, are highly dependent on their congener-specific activities such as those mediated through activation of the aryl hydrocarbon (Ah) receptor (*2*). Thus, knowledge of the PCB and PCDD/F congener composition in environmental matrices can help in predicting and quantifying their toxicities. Although there has been much work in determining the spatial distribution and temporal stability of PCBs in river sediments, the water column, and selected biota along the main-stem Hudson River (*7, 8, 16*−*18*), rarely have spatial patterns of tPCBs and individual congeners been quantified in a single species.

There has been less work done on PCDD/F contamination levels in sediments and biota of the Hudson River estuary.

10.1021/es034177f CCC: $27.50
Published on Web 01/08/2004

TABLE 1. Sample Collection and Meristic Data for YOY (Y) and Adult (M) Atlantic Tomcod Sampled from the Main-Stem Hudson River, NY, Newark Bay, NJ, Hackensack River, NJ, and Miramichi River

sample ID	month/year	site name	RM	composite no.	male (m)/female (f)	length (cm)	age (years)
M50(m)	12/1997	Garrison	50	10	m	23.7 ± 1.7	2
M50(f)	12/1997	Garrison	50	10	f	27.0 ± 1.4	2
M-2(m)	12/1996	Hackensack R.	1−3[a]	6	m	18.5 ± 2.7	1−2
M-2(f)	12/1996	Hackensack R.	1−3[a]	11	f	19.5 ± 1.7	1
Y-2	08/1998	Hackensack R.	1−3[a]	8			<1
Y-1	08/1998	Newark Bay	proper	10			<1
Y1	08/1998	Battery	1	9			<1
Y8	08/1998	Manhattan	8	10			<1
Y10	08/1998	Manhattan	10	10			<1
Y17	08/1998	Yonkers	17	9			<1
Y37	08/1998	Haverstraw Bay	37	5			<1
Y58	08/1998	Moodna Cr.	58	9			<1
Y67	08/1998	Poughkeepsie	67	8			<1
Y77	08/1998	Mid-Hudson	77	10			<1
Y82	08/1998	RM82	82	10			<1
M50(f)[b]	01/1999	Garrison	50	10	f	18.4−25.5	>1
Mmir(f)[b]	01/1999	Miramichi R[c]	18[d]	5 × 4−5	f	21.5−31.5	>1
Y0	09/2000	Battery	0	5			<1
Y17[e]	09/2000	Yonkers	17	1			<1
Y37	09/2000	Haverstraw Bay	37	5			<1
Y43	09/2000	RM43	43	5			<1
Y50	09/2000	Garrison	50	5			<1
Y80	09/2000	RM80	80	5			<1
Y85	09/2000	RM85	85	3			<1
Y91	09/2000	Kingston	91	1			<1
Y96	09/2000	RM96	96	1			<1
Y107	09/2000	Catskill	107	1			<1

[a] Distance from the confluence of the Hackensack River with Newark Bay. [b] Unfertilized egg samples were also collected from these fish. [c] Captured at Loggieville, NB, Canada (reference site). [d] Distance upstream from Miramichi Inner Bay barrier islands. [e] Low lipid weight.

We are unaware of any studies that have quantified tPCDD/Fs and characterized its congener pattern in a single species throughout its distribution with the Hudson River estuary. The lower Passaic River, NJ, one of two major tributaries of Newark Bay, was designated a U.S. Federal Superfund site because of the deposition of large amounts of PCDD/Fs, particularly 2,3,7,8-TCDD, from Diamond Alkalai Co. (subsequently known as the Diamond Shamrock Chemical Co.) that manufactured the herbicides 2,4,5-trichlorophenoxyactic acid (a major component of Agent Orange) and its esters and amines from 1951 to 1969. As a result, it has been estimated that in total 4−8 kg of TCDD was deposited in Newark Bay sediments by downstream transport from this source (*19*). Bioaccumulation of high levels of 2,3,7,8-TCDD/F in striped bass and blue crabs (*Callinectes sapidus*) from the Newark Bay complex has been documented (*20*). O'Keefe et al. (*21*) examined TCDD/F concentrations in striped bass, finding 2,3,7,8-TCDD/F in much greater concentrations in striped bass from several sites in the Hudson River estuary, including Newark Bay and RM 77 main-stem Hudson River, compared to those from the Chesapeake Bay, western Long Island Sound, NY, and Rhode Island coastal waters. Bopp et al. (*22*) also reported that high levels of sediment-borne PCDDs, primarily OCDDs, were deposited in the upper main-stem Hudson River (above RM 150) from about 1960, perhaps from combustion sources.

Atlantic tomcod *Microgadus tomcod* is an abundant, bottom-dwelling fish species in Atlantic coast estuaries with spawning populations extending from the Hudson River to Labrador. Tomcod is the only wintertime spawner among Hudson River finfish species, and as a result, young life stages serve as important prey to commercially important resource species such as striped bass (*23*). Tomcod spawn near or above the freshwater−saltwater interface (usually from RM 25 to RM 75 in the Hudson River), and although adults and juveniles move throughout the lower estuary (from RM 0 to RM 125), they probably do not move into coastal waters (*24*). Previous work showed that tomcod may serve as a sensitive sentinel species for polyhalogenated (PHAH) and polynuclear (PAH) aromatic hydrocarbon contamination in Atlantic coast estuaries, including the Hudson River. This research was based on levels of PAH metabolites in bile, hepatic cytochrome P4501A1 (CYP1A1) mRNA expression, and overall hepatic DNA damage (*25*). Evidence of the sensitivity of this model to environmental degradation is the prevalence of hepatocellular carcinomas that at one time exceeded 90% in older Hudson River tomcod (*26*). However, more intensive and recent studies of the spatial patterns of CYP1A1 mRNA expression in environmentally exposed YOY tomcod from the Hudson River (*27*) and in adult tomcod that were chemically treated with PCBs and TCDD (*28, 29*) suggest that resistance to these xenobiotics may have developed in the Hudson River population. This work examines PCB and PCDD/F totals and normalized congener patterns in hepatic tissues of YOY and adult tomcod collected from various sites in the main-stem Hudson River and the adjacent Newark Bay complex including the Hackensack River. This work was undertaken in order to examine spatial and age-related variability in levels and patterns of PCBs and PCDD/Fs in this sentinel species in the Hudson River estuary. Additionally, this information may provide some insight into the dynamics and potential sources of these contaminants for Hudson River fishes.

Materials and Methods

Sample Collection. Mature (1 year and older) male and/or female tomcod were collected with unbaited box traps during spawning season in December 1996 and 1997 and January 1999 at RM 50 in the main-stem Hudson River and/or the Hackensack River. YOY tomcod of unknown gender were collected in the summer months between 1998 and 2000 with bottom trawls at various points along the main-stem Hudson River, Hackensack River, and Newark Bay as indicated in Table 1 (see Figure 1 for map). Adult female tomcod were collected in January 1999 with smelt bag nets in the Miramichi River, NB, an estuary free of any known

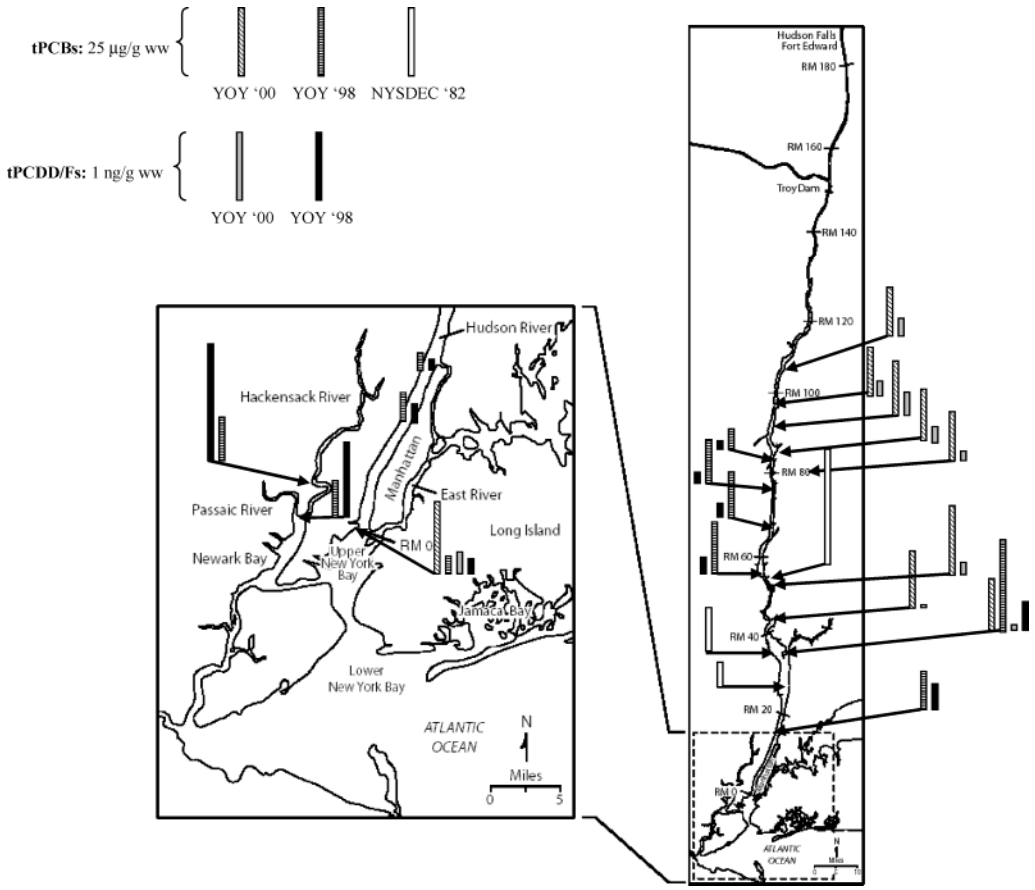

FIGURE 1. Map of the Hudson River, NY, with an insert of the lower estuary showing Newark Bay/Hackensack River, NJ. Samples taken at Newark Bay 1−3 miles up Hackensack River, and Hudson River Miles, 0, 8, 10, 17, 37, 43, 50, 58, 67, 77, 80, 82, 85, 91, 96, 107. Bars indicate tPCB and tPCDD/Fs (ww) in young-of-the-year (YOY) tomcod liver collected in 1998 and 2000 for this work and in 1982 for PCBs only by New York State Department of Environmental Conservation (NYSDEC) (*30*). NOTE: Y17^{e} was not included due to its unusual congener pattern and abnormally low lipid content compared with all other YOY samples.

point sources of PCBs, although levels of PCDD/Fs in its biota were a concern because of the one-time presence of a bleached kraft pulp and paper mill.

Sample Preparation for Contaminant Analysis. Fish were sacrificed immediately after capture, their livers excised, snap frozen in liquid nitrogen, and stored at −70 °C. Livers were pooled and homogenized using a Sorvall Omni-Mixer (Ivan Sorvall Inc., Newtown, CT) (see Table 1 for composite number which refers to number of fish pooled in each sample). If sample weights permitted, an aliquot was taken for analyses of percent lipid (gravimetry of lipid extraction) and moisture (oven drying). Lipid results were not used to normalize the data since the sample amounts of several YOY livers were insufficient for a lipid analysis to be conducted.

Methods used for PCB and PCDD/F determinations are based on Environment Canada's protocol for the determination of PCDDs and PCDFs in pulp mill effluents EPS1/RM/19 and the U.S. EPA's Method 1613 and have been published in Ikonomou et al. (*31*). In brief, approximately 6 g-wet weight (ww) of adult liver, 10 g-ww of unfertilized eggs, or 1 g-ww of YOY tomcod liver were spiked with various ^{13}C-labeled surrogate internal standards for quantitation purposes. Samples were dried with anhydrous sodium sulfate (Na_2SO_4) and extracted with 1:1 dichloromethane(DCM): hexane in a gravity column. The extracts were reduced by rotary evaporation, loaded onto gel permeation chromatography (GPC) cleanup columns, and eluted with 1:1 DCM: hexane. Samples were taken through two additional cleanup stages, silica and alumina columns, to eliminate polar and/or pigment substances that may contribute to matrix interference during analysis. The cleaned-up samples were then fractionated using carbon fiber high-performance liquid chromatography: fraction I (di-*o*-PCBs), fraction II (mono-*o*-PCBs), fraction III (non-*o*-PCBs), and back-flushed fraction IV (PCDD/Fs).

HRGC−HRMS Analysis. Fractions I, II, and III/IV (combined as non-*o*-PCB 169 elutes over fractions III and IV) were analyzed by HRGC−HRMS using a 60 m DB-5 fused silica capillary column (0.25 mm i.d. with 0.1 μm film thickness) and positive EI conditions with an ionization voltage of 28−35 eV. Two or more ions, M^+ and $(M+2)^+$, of known relative abundance were monitored for each molecular ion cluster representing a group of isomers and two for each of the ^{13}C-labeled surrogate standards for each group. Instrument stability and relative response factor variance were obtained from the analysis of calibration standard solutions during each sample batch. The concentrations of identified compounds and their limit-of-detection (LoD) were calculated by the internal standard method using mean relative response factors of calibration standard solutions run as described in Ikonomou et al. (*31*). Reported concentrations were recovery corrected based on the recovery of representative $^{13}C_{12}$-labled surrogate standards for each chlorohomologue group (i.e., $^{13}C_{12}$-tetra through $^{13}C_{12}$-octa dioxins and $^{13}C_{12}$-tetra through $^{13}C_{12}$-hepta furans, and various $^{13}C_{12}$-tri through $^{13}C_{12}$-deca PCBs). Additionally QA/QC measures included running a procedural blank (final values are blank subtracted), replicate, and certified or other reference material with each batch of nine samples.

See Supporting Information Tables 1 and 2 for full congener PCB and PCDD/F data, respectively, along with a description of the data treatment process.

Hierarchical Cluster Analysis (HCA) and Direct Mixing Model (DMM). HCA was performed using Pirouette version 2.7 (Infometrix, Woodinville, WA) on the 100% normalized data, which was additionally autoscaled/standardized to remove weighting based on the abundance of each congener. Distances between clusters are shown in Euclidean distance. The farthest-neighbor linkage method ("Complete Link" in Pirouette) was used, and it yielded similar clusters as the centroidal linkage method. The Y17 (collected in 2000) sample was removed from this analysis due to its unusual congener pattern and abnormally low lipid content compared with other YOY samples.

The Aroclor composition of each sample was modeled using a direct mixing model (DMM) developed by Sather et al. (*32*). The DMM uses an iterative technique involving a matrix of linear equations constructed from the 100% normalized congener profiles of Aroclor standards A1242, A1254, and A1260 determined by GC−HRMS as per Ikonomou et al. (*31*). The procedure involves iterations of a theoretical congener profile obtained by matrix multiplication, controlled by minimization of the residual sum-of-squares (RSS) between the 100% normalized congener profile of the sample and that of the predicted composition. As geochemical, bioaccumulative, and metabolic factors all serve to obscure original PCB source patterns in biological tissues, DMM aroclor composition results should be interpreted with caution. In this work, this tool was not intended to provide an absolute estimate of potential sources but more as a semiquantitative method to characterize hepatic PCB patterns with respect to the three most commonly used aroclor formulations.

Results and Discussion

Overall Levels of PCBs and PCDD/Fs in Tomcod from the Hudson River and Miramichi River Estuaries. Hepatic tPCBs and tPCDD/Fs in YOY tomcod of unknown gender collected in 1998/2000 from the main-stem Hudson River, NY (RM 0−107), and from Newark Bay/Hackensack River, NJ, ranged from 7 to 34 μg/g-ww and from 43 to 1736 pg/g-ww, respectively (Figure 1). Liver composites ($n = 10$) from adult female and male fish collected in 1997 at Hudson River RM 50 showed tPCBs of 4.4 and 21.5 μg/g-ww and tPCDD/Fs of 161 and 351 pg/g-ww, respectively. Adult female ($n = 6$) and male ($n = 11$) tomcod sampled in 1997 from the Hackensack River, NJ, showed tPCBs of 4.0 and 12.3 μg/g-ww and tPCDD/Fs of 573 and 1178 pg/g-ww, respectively. Adult male tomcod showed hepatic PCB and PCDD/F burdens (ww) that were 2−5 times greater than females collected at the same location and time. Lower concentrations of total coplanar PCBs and tPCDDs/Fs in females than males reflects, at least in part, offloading of lipophilic organochlorine contaminants into eggs (*15*) as reported for other fish species (*33*, *34*). These tPCB values were much greater than the average value found in adult tomcod from the Miramichi River (Mmir(f)[b]; our PCB reference site) of 0.11 ± 0.07 μg/g.

Temporal Variation of PCBs in Adult Tomcod from the Main Stem Hudson River. Klauda et al. (*9*) reported whole body tPCB concentrations in adult tomcod (mixed sex) collected in 1978 from the spawning areas near RM 50 on the main-stem Hudson River of 0.01−0.67 μg/g-ww and liver concentrations that ranged from 15.1 to 98.2 μg/g-ww and averaged 37.5 μg/g-ww. Similarly, Dey et al. (*26*) reported that hepatic concentrations of tPCBs in adult tomcod (mixed sex) collected in 1983−84 from the main-stem Hudson River at RM 50 ranged between 2.5 and 38.2 μg/g-ww with a mean concentration of slightly more than 30 μg/g-ww in the oldest (age 2+) fish. The mean hepatic tPCB burden in our pooled samples of male and female adult tomcod collected in 1997 at RM 50 was 12.7 μg/g-ww. From this comparison, we report a reduction over the past two decades in hepatic tPCB burdens in tomcod from RM 50 on the main stem of the Hudson River. Furthermore, tPCB levels in the livers of adult tomcod collected in 1982 by the NYSDEC at RM 25 and RM 36 were similar to those we found in the livers of YOY fish collected in this work at nearby locations; however, the tPCB level at RM 50 in 1982 was significantly greater than that which we detected in the current study (see Figure 1). It must be noted that Butcher et al. (*35*) showed that NYDEC's 1979 and 1983 Aroclor-based methods consistently underestimated PCB totals by 13−15% compared to the congener-specific method which was used in this work, so the true reduction in hepatic tPCB may be even greater at RM 50 than indicated by Figure 1. Although the tPCB levels at RM 50 have clearly diminished over the last two decades, a similar trend was not observed, based on available data, at lower RMs (i.e., RM < 40) where lower Hudson River sources, such as sewage effluents, may still be a significant source of PCBs to the Hudson River ecosystem.

Spatial Variation of Hepatic PCB and PCDD/F Levels in YOY Tomcod. YOY tomcod have presumably moved far less than their adult counterparts and, thus, may better represent the local contaminant levels where they were captured. Levels of hepatic tPCBs and tPCDD/Fs in YOY tomcod collected in Newark Bay/Hackensack River (RMs −2−0) and the main-stem Hudson River (RMs 0−107) exhibited significant spatial heterogeneity. Our results differ from those of Monosson et al. (*13*), who failed to observe spatial heterogeneity in tPCBs in killifish (*Fundulus heteroclitus*) collected from three sites in the lower Hudson River estuary, Newark Bay, Piermont Marsh (RM 25), and Iona Island Marsh (RM 45), despite their very limited home range. Hepatic concentrations of tPCBs in the main-stem Hudson River showed slightly increased concentrations between RM 37 and 50 compared to samples taken at other river miles. Among four sediment samples collected in August 1993 between RM 25 and RM 100 by the USEPA (*36*), the station at RM 47.3 (Iona Island) had the highest tPCB level which may be reflected in our study by the highest levels seen in this region.

Hepatic concentrations of tPCDD/Fs in YOY tomcod from the Hudson River estuary were by far highest in fish collected at Newark Bay/Hackensack River. Levels of tPCDD/Fs in YOY tomcod from Newark Bay/Hackensack (1109−1736 ppt ww) are among the highest ever reported in natural populations of any species to our knowledge. These levels of hepatic PCDD/Fs far exceed those known to elicit early life toxicity in several sensitive species of freshwater fish (*37*) and in Atlantic tomcod (Chambers and Wirgin, unpublished data). YOY tomcod collected in the main stem of the Hudson River showed much lower levels of tPCDD/F, with slight increases seen at RMs 37 and 91.

YOY Tomcod as Site-Specific Monitors of Organochlorine Contamination. HCA was used to determine if congener-specific hepatic PCB patterns in YOY tomcod could be used to group tomcod based on exposure histories and locations of capture. The YOY fish grouped into three clusters at a similarity level of 0.4 (see Figure 2). The Hudson cluster A included Y1−Y17 and the Newark Bay/Hackensack River samples. The Hudson cluster B included Y37−Y77, although Y0, which also grouped in this cluster, was considered an outlier to this group due to its distinct location from the others in this group. Finally, the Hudson cluster C consisted of Y80−Y107 with Y37 and Y50 as outliers. Due to the inherently large variability associated with biological samples as opposed to abiotic environmental samples (i.e., sediments), the presence of outlier samples is not unusual. Despite these anomalous samples, it appears that YOY tomcod may serve as site-specific indicators of the levels and congener-specific patterns of PHAH contaminants. Within the adult cluster (Figure 2), the greatest difference in pattern occurred between tomcod from RM 50 main-stem

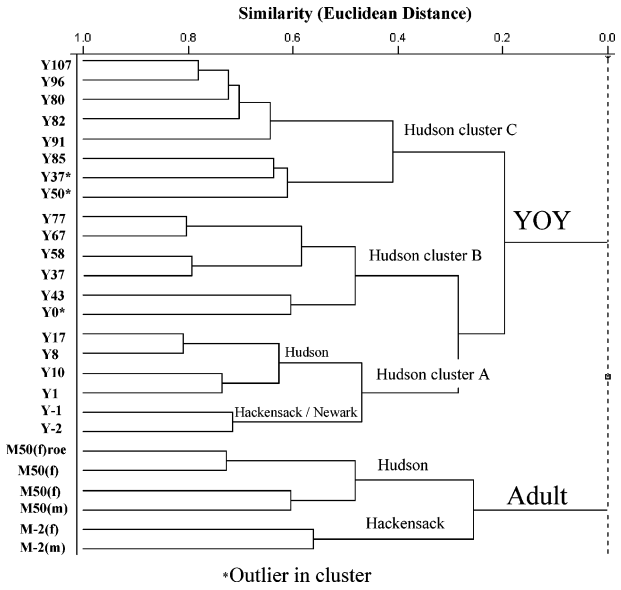

FIGURE 2. Hierarchical cluster analysis dendrogram using farthest-neighbor linkage method on normalized YOY and adult hepatic PCB compositions. Y17[e] was excluded from this analysis.

Hudson River and those from Newark Bay/Hackensack River, indicating that the adult tomcod also show a certain degree of site-specificity in PCB patterns. Additionally, the pattern in the egg sample was found to be most similar to that of their mother's (i.e., M50(f)), supporting the idea that adult female tomcod unload lipophilic contaminants directly into their eggs.

Comparison of Hepatic PCB Congener Profiles in YOY and Adult Tomcod. Hepatic PCB congener composition differed dramatically between YOY and adult fish. Figure 3 shows specific PCB compositional differences between the livers of YOY and adult tomcod in the 50 most prevalent congeners detected. The di- to tetrachlorinated biphenyls dominated the composition of PCB congeners in YOY tomcod, whereas the penta- to nonachlorinated biphenyls predominated in adults with particular prevalences of the 2,4,5-substituted diortho congeners, BZ#s 99, 138, 146, 153, 170, 180, 183, 187, 194, 201, 203, 206. This 2,4,5-substitution makes these congeners exceptionally recalcitrant to biotransformation/elimination in biota (*39*), including fish (*40*).

We suggest at least three different factors as possible causes for the differences seen in PCB congener composition between YOY and adult fish. First, it is possible that the diet of tomcod in the Hudson River shifts between invertebrates in small YOY fish to more piscivorous food items in adults and that PCB congener profiles differ between invertebrate and vertebrate prey. However, several studies have demonstrated that the diet of both YOY and adult tomcod in the Hudson River consists almost exclusively of invertebrate prey, primarily calanoid copepods, gammarids, *Neomysis* sp., polychaetes, and *Monoculodes* (*41*, *42*). However, it has also been shown that a dietary shift occurs from zooplankton to macroinvertebrates in the first year of life of Hudson River tomcod. Similarly, small juvenile tomcod from the Miramichi River consume exclusively copepods and mysids, whereas the diet of adults consists almost exclusively *Crangon* sand shrimp, at least at certain times of the year (Courtenay, unpublished data). Because zooplankton are distributed only within the water column, the overall levels and patterns of PCB and PCDD/F congeners which they bioaccumulate probably differ from that of benthic macroinvertebrate prey in that waterborne PCBs and PCDD/Fs are usually dominated by lesser substituted congeners than those in sediments.

Second, the longer existence and greater mass of adults compared with the YOY fish are known to augment the effects of bioaccumulation and metabolic transformation and elimination in adult fish. This in turn may skew the PCB composition in adults, resulting in the most recalcitrant and highly bioaccumulative congeners dominating the composition.

Finally, it is possible that the capacity of tomcod to metabolize and eliminate PCBs differs between younger and older life stages. If true, our data would suggest that older fish are less able to metabolize select higher-chlorinated PCB congeners than YOY tomcod. There is some evidence supporting the possible occurrence of this phenomenon in tomcod from polluted rivers. Controlled laboratory studies have demonstrated that CYP1A1 mRNA induction is 2 orders of magnitude more sensitive to PCB77s in larval compared to adult tomcod from the Hudson River (*15*). Also, Couillard et al. (manuscript in preparation) observed significant differences in CYP1A1 mRNA and protein expression between younger and older environmentally exposed adult tomcod from the polluted St. Lawrence River. Taken together, the PCB congener patterns and CYP1A1 expression data suggest

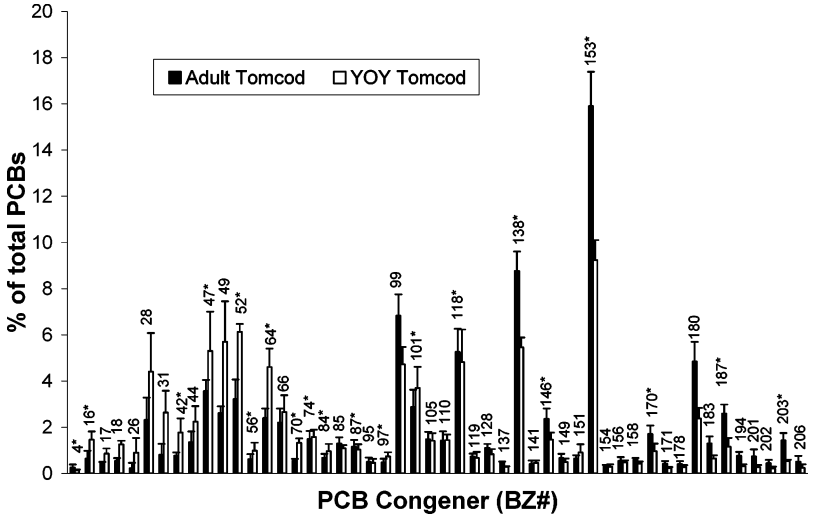

FIGURE 3. Normalized patterns of the 50 most prevalent PCB congeners in YOY tomcod livers ($n = 5$) compared to that in adult tomcod livers ($n = 5$) collected at similar locations in the lower Hudson River and adjacent Newark Bay/Hackensack River between 1997 and 2000. Error bars are in units of standard deviation. Asterisk (*) denotes coeluting congener group with most abundant congener listed based on preferential substitution patterns in Aroclor production via electrophilic aromatic substitution mechanisms (*38*).

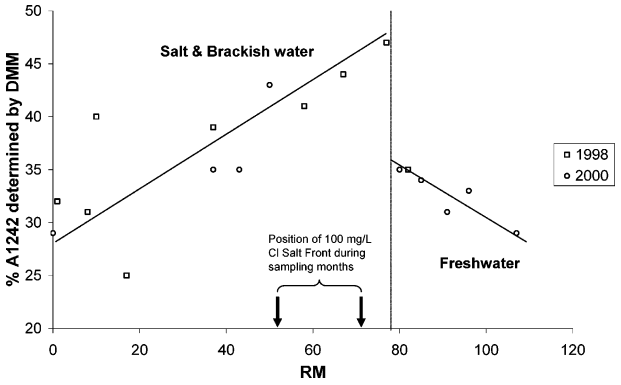

FIGURE 4. Percent A1242 characteristic as determined by a direct mixing model (DMM) from the normalized PCB congener pattern in YOY tomcod from various locations on the main stem of the Hudson River (coefficient of determination (r^2): salt and brackish = 0.471; freshwater = 0.618).

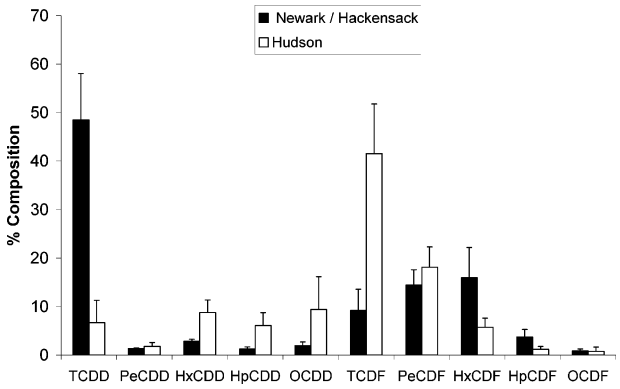

FIGURE 5. Normalized hepatic PCDD/F chlorohomolgue patterns in male/female, adult, and YOY pooled tomcod from the main-stem Hudson River (n = 22) and Newark Bay/Hackensack River complex (n = 4). Error bars are in units of standard deviation.

that either natural selection or a physiological acclimation response may reduce metabolism of PCBs and alter resulting congener profiles in older age groups of tomcod from highly polluted sites.

Aroclor Compositions and Spatial Trends. The direct mixing model (DMM) validated in Sather et al. (*32*) and Ikonomou et al. (*43*) was used to characterize full congener PCB patterns in the YOY tomcod sampled in 1998 and 2000 in terms of aroclor compositions of A1242:A1254:A1260 (Supporting Information, Table 3). In most cases, a 1:1:1 (A1242:A1254:A1260) composition best characterized the hepatic profiles, particularly in tomcod from the lower RMs. This is consistent with the EPA's reassessment report (*8*) which based on dated sediment cores concludes that the PCB loads to the saline lower Hudson River are a mixture of upper Hudson River sources (i.e., A1242) with significant contributions of heavier Aroclors (A1254 and A1260) from sewage treatment plants located down-river in the NY/NJ Harbor region.

Figure 4 shows the percent A1242 characteristic in the hepatic PCB profiles with river mile. A1242 is known to be the predominant PCB input from the former capacitor plants in the upriver Hudson River and more recently from sediments in the Thompson Island pool where much of the A1242 deposited (*8*). This spatial trend shows an increasing A1242 contribution with RM until about RM 80, where an unexpected shift in pattern occurs. Tomcod caught beyond this point show a much lower and decreasing A1242 contribution with river mile. The positive linear trend seen between RM 0 and 80 was significant at a 95% confidence level, whereas the negative linear trend between RM 80 and 107 was only significant at a 90% confidence level. To attempt to explain this observed shift, trends in water chemistry of the Hudson River were explored. The most obvious finding was that this shift to a lower composition of lesser-chlorinated congeners occurs near a region of transition from brackish water to freshwater. This region is best defined by the salt front, which may be considered the point in the river at which the conductivity begins to increase exponentially from freshwater values and is generally associated with a chloride level of 100 mg/L (*44*). The salt front in the Hudson River is generally found near RM 50 but varies intra- and interannually based on tidal currents, wind, basin morphometry, and freshwater flows, two-thirds of which are controlled by the Troy Dam (*45*).

The YOY in this work were sampled from mid to late summer when salinity in the Hudson River is characterized by upriver maxima in saltwater intrusion due to low freshwater flows, and thus, the salt front could have occurred as far upriver as RM 80. During the August 1998 and September 2000 months of sampling (YOY only), the salt-front occurred between RM 64 and 70 and RM 51 and 72, respectively (*46*). It is known that octanol−water partition coefficients (K_{ow}) for PCBs are lower in freshwater than in saltwater (*8*), and therefore, shorter half-life congeners (i.e., low chlorinated = low K_{ow}) will partition into freshwater from tissues to a greater extent than in saltwater. This effect would be greatly diminished in higher-chlorinated congeners due to their longer half-lives and generally higher retention in biota. Thus, although tomcod caught below RM 80 exhibit a predicted %A1242 composition proportional to their distances from upper Hudson River A1242 sources, those caught above RM 80 may have depurated a significant amount of the lower-chlorinated congeners which make up a large percentage of the A1242 upstream source (i.e., primarily tri- and tetrachlorinated biphenyls). Alternately, these animals may have assimilated a lesser amount of lower-chlorinated congeners due to the decreased partitioning of PCBs into lipid in freshwater versus saltwater, which would be expected based on the reduction in K_{ow} of PCBs in freshwater, as mentioned previously.

PCDD/Fs in Hudson River and Newark Bay/Hackensack River Tomcod. Contrary to what was seen with PCBs, HCA on the PCDD/F chlorohomologue and semi-congener-specific compositional profiles showed no apparent distinctions between adult female and male tomcod or between YOY and adult tomcod collected at similar locations. This result may be due to the fact that PCDD/Fs octanol−water partition coefficients (K_{OW}), the log of which varies from ~6.5 to 9 (*47*) for the chlorohomologues measured in this work (i.e., from tetra to octa), do not span as great a range into the optimum bioaccumulation zone as do those of PCBs, log K_{ow} ~4.5−8 for di−deca congeners (*48*), and thus, differences due to sex and age may go undetected. Thus, the following discussion on chlorohomologue and congener PCDD/F patterns is based on pooled age and sex data.

Large differences were seen between the chlorohomologue composition of PCDD/Fs of tomcod sampled in Newark Bay/Hackensack River and that of those collected along the main stem of the Hudson River (see Figure 5). Additionally, tPCDD/F levels in the livers of YOY tomcod collected in the Hackensack River and Newark Bay, 1736 and 1109 pg/g-ww, respectively, were much higher than those in tomcod collected from the main-stem Hudson River, which ranged from 43 to 425 pg/g-ww (excluding outlier Y17[e]) (Figure 1). As seen in Figure 5, TCDD predominated the composition of the Newark Bay/Hackensack River samples, making up almost 50% of the total PCDD/Fs. Upon more detailed examination of the TCDD congeners in these samples, this group was found to consist almost exclusively of 2,3,7,8-

TCDD. The likely source of 2,3,7,8-TCDD in the Hackensack River/Newark Bay is discharge from the Diamond Alkali Co., which manufactured Agent Orange in the Newark Bay region between 1951 and 1969 (*49*). Conversely, the PCDD/F chlorohomologue profile found in tomcod from main-stem Hudson River was dominated by TCDF, which consisted of 30−100% 2,3,7,8-TCDF (including its potential coeluters on a DB-5 column) which is a co-contaminant in PCB formulations (*21*), a major PCDD/F formed in the combustion of PVC (*50*), and a byproduct formed in the chlorine bleaching of wood pulp (*51*).

The spatial variation in PCB and PCDD/F patterns in YOY tomcod indicate that this species may serve as an effective time-integrated biomonitor of site-specific organochlorine contamination. Additionally, the upstream A1242 source was detected in tomcod at a composition relative to the distance caught upstream in the salt and brackish water zone (i.e., <RM 80). However, upon entry into freshwater, this A1242 source fingerprint diminished somewhat, possibly due to the depuration of the predominantly lower-chlorinated congeners into the freshwater environment. The PCDD/F congener profile comparison between Newark/Hackensack and Hudson River revealed a distinct 2,3,7,8-TCDD source in the former location which likely was due to the herbicide production facility that previously operated there.

Acknowledgments

We thank Grace Maxwell, Paul Kelly, and Brian Kelly for help in obtaining samples from Miramichi. We also thank Mark Mattson and the crews of Normandeau Associates for their help in tomcod collections. Additionally, we would like extend our thanks to all the chemists from the Regional Dioxin Lab, DFO, involved in processing and analyzing the samples for this work. This work was supported by a DFO Environmental Sciences Strategic Research Fund grant to S.C. We acknowledge support of the Hudson River Foundation, NIEHS Grant ES10344, and NIEHS Center Grant ES00260. The constructive comments of the anonymous reviewers are much appreciated; they helped us in improving the clarity of this publication.

Supporting Information Available

Two tables of full congener PCB and PCDD/F data, data treatment details, and one table of DMM results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review February 26, 2003. Revised manuscript received November 20, 2003. Accepted December 2, 2003.

ES034177F