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Uptake of Planar Polychlorinated Biphenyls and 2,3,7,8-Substituted Polychlorinated Dibenzofurans and Dibenzo-*p*-dioxins by Birds Nesting in the Lower Fox River and Green Bay, Wisconsin, USA

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Abstract. The uptake of persistent polychlorinated hydrocarbons (PCHs) by four avian species was investigated at upper trophic levels of two aquatic food chains of the lower Fox River and Green Bay, Wisconsin. Accumulation of total and specific planar polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxin (PCDDs), and H4IIE rat hepatoma cell bioassay-derived 2,37,8-tetrachlorodibenzo-*p*-dioxin equivalents (TCDD-EQ) was evaluated in Forster's tern (*Sterna forsteri*) and common tern (*Sterna hirundo*) chicks, and in tree swallow (*Tachycineta bicolor*) and red-winged blackbird (*Agelaius phoeniceus*) nestlings from colonies nesting in several locations within the watershed. Concentrations of the PCHs were greatest in eggs and chicks of the two tern species, less in the tree swallows and least in the red-winged blackbirds. Young of all four species accumulated total PCBs, PCB congeners 77, 105, 126, and 169, and TCDD-EQ. The young birds also accumulated small concentrations of several 2,3,7,8-sbustituted PCDF and PCDD congeners. Uptake rates for certain of the PCHs for the Forster's tern chicks were: 15 μg/day for total PCBs, 70, 200, 6.5, and 0.14 ng/day for PCB congeners 77, 105, 126, and 169, respectively, and 270 pg/day for TCDD-EQ. Principal components analysis revealed that the patterns of PCH concentrations in the samples were influenced by species of bird, their age (or length of exposure) and nesting location. Collectively, our findings demonstrate that exposure of avian species to contaminants derived from aquatic food chains can be characterized and quantified for the purposes of ecological risk assessment.

Persistent bioaccumulative polychlorinated hydrocarbons (PCHs) continue to be of concern in the Great Lakes ecosystem. Because of their demonstrated toxicity and potential for additive effects, PCHs of particular consequence are planar non ortho- or mono ortho-substituted polychlorinated biphenyls (PCBs) and 2,3,7,8-substituted polychlorinated dibenzofurans (PCDFs) and dibenzo-*p*-dioxins (PCDDs) (Poland and Knutson 1982; Tanabe *et al.* 1987; Safe 1990). These PCHs have been suggested as a causative agent in adverse effects observed in several Great Lakes fish and wildlife populations including mink (Aulerich *et al.* 1973; Wren 1991), lake trout (Mac 1988; Walker et al. 1991) chinook salmon (Ankley *et al.* 1991), and a number of colonial fish-eating bird species such as Forster's tern and double-crested cormorant (Kubiak *et al.* 1989; Gilbertson *et al.* 1991; Tillitt *et al.* 1992).

Because of atmospheric deposition and internal recycling, PCHs are ubiquitous contaminants of sediments throughout the Great Lakes ecosystem (Eisenreich *et al.* 1981); however, as a result of point-source inputs, concentrations of these contaminants are particularly great in sediments in Areas of Concern (AOC) identified by the International Joint Commission, such as the Saginaw River and Bay, Michigan and the lower Fox River and Green Bay, Wisconsin (Hileman 1988; Michigan Department of Natural Resources 1988; Ankley *et al.* 1992). Despite general elevation of concentrations of PCBs, PCDFs, and PCDDs in biota from various AOC sites, it can be difficult to characterize exposure of fish and wildlife for the purposes of ecological risk assessment and the subsequent design of effective remediation strategies. For example, because some avian species migrate, it often is difficult to define the extent to which observed concentrations of contaminants are derived from the system of concern. This is particularly true when the exposure history of a group of animals is completely unknown, such as in the case of birds that migrate hundreds or thousands of kilometers and overwinter in South America.

In quantifying site-specific exposure, it is desirable to evaluate the life stages that are expected to exhibit the greatest

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potential for contaminant uptake; in most birds this is the rapidly growing young. By focusing efforts on monitoring during the nesting season and by comparison of concentrations of chemicals in eggs and prefledge young, rates of contaminant uptake at specific sites can be calculated (Niemi *et al.* 1986; Custer *et al.* 1991; Scharenberg 1991). An added benefit of monitoring young birds is that this is a highly sensitive life stage with regard to toxicity of PCHs such as PCBs and PCDDS (Higginbotham *et al.* 1968; Brunström 1988; Brunström and Anderson 1988).

The objective of our study was to quantify site-specific PCH exposure of four avian species representing at least two different aquatic food chains. Uptake of PCBs, PCDFs and PCDDs was evaluated in the young of four species of birds nesting along the lower Fox River and Green Bay, Wisconsin: Forster's tern (*Sterna forsteri*), common tern (*Sterna hirundo*), tree swallow (*Tachycineta bicolor*), and red-winged blackbird (*Agelaius phoeniceus*). These species all have the potential for significant exposure to PCHs via aquatic food chains. Both of the tern species are primarily piscivores, while tree swallows and red-winged blackbirds are insectivores whose diets can consist of emergent aquatic insects such as chironomids or odonates (Orians 1961; Wilson 1978; Quinney and Ankney 1985; Cohen and Dymerski 1986). Also, the same Forster's tern colony investigated in this study has had documented adverse reproductive impacts that were correlated with exposure to planar PCBs (Hoffman *et al.* 1987; Kubiak *et al.* 1989). In addition to quantifying the uptake of PCBs, PCDFs, and PCDDs in young birds, we utilized the H4IIE rat hepatoma cell bioassay to evaluate the relative toxic potency of the entire PCB/PCDF/PCDD mixture in the samples (Jones *et al.* 1993). This enabled an integrated measure of the potential toxicity of the mixture expressed as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TCDD-EQ) (Safe *et al.* 1989; Tillitt *et al.* 1991a, 1991b). Finally, to characterize patterns of PCBs, PCDFs, and PCDDs observed in eggs and young from the four different species, concentrations of the PCHs were subjected to principal components analysis (Wold *et al.* 1984; Niemi *et al.* 1986).

Materials and Methods

Eggs and young of the four species were collected in the spring and summer of 1988 from several locations in the low Fox River and Green Bay system (Figure 1). Forster's and common terns were collected from colonies nesting on a dredged sediment confined disposal facility (CDF) at the mouth of the lower Fox River named Renard (or Kidney) Island (Harris *et al.* 1993). Samples of tree swallows were collected from artificial nest boxes placed on the CDF and at sites along the lower Fox River (Beaver and Lederle 1989). Red-winged blackbirds were collected from three sites directly adjacent to Green Bay, as well as from three inland wetlands remote from the river or the bay (Rothstein *et al.* 1989).

An important part of the overall study design was to evaluate reproductive success of the four species; those results as well as further information concerning sample collection are given elsewhere (Beaver and Lederle 1989; Rothstein *et al.* 1989; Harris *et al.* 1993). Forster's tern eggs initially were collected from six nests for the instrumental quantification of the PCHs and the H4IIE assays; these same nests then were sampled for chicks at various stages of fledging. A total of 11 chicks, ranging in age from 3 to 27 days, were collected. Because of predation, samples of common tern eggs were collected only from four nests; four chicks ranging in age from 5 to 16 days were collected from these same nests. There was sufficient mass of all the tern eggs and chicks to enable instrumental quantification and H4IIE assays to be performed on individual nonpooled samples. However, in the case of the tree swallows and red-winged blackbirds, egg samples were pooled by site to provide a sufficient mass of material for all of the analyses. For the tree swallows, a composite of seven eggs was collected from the CDF, while a composite of 19 eggs was collected from the river site. We also pooled the tree swallow nestlings to provide adequate sample mass. From the CDF, three nestlings aged 9, 13, and 17 days were pooled, while three composites of four nestlings each were collected 4, 8, and 16 days posthatching from the river site. Composite samples of the red-winged blackbird eggs consisted of 10, 4, and 5 eggs from the three inland sites, and 3, 8, and 8 eggs from the bay sites. Individual red-winged blackbird nestlings, approximately 10 days in age, also were collected from each of the study sites; each nestling provided enough biomass to be analyzed individually.

Shells of eggs were removed upon collection and the contents placed in solvent-rinsed glass containers; the young birds were euthanasized and placed in solvent-rinsed glass containers or wrapped in foil. All samples were weighed to the nearest 0.1 g and stored frozen until homogenized. Chick or nestling samples were partially thawed and homogenized in a Waring blender, while the egg samples were thawed and homogenized with a variable-speed drill fitted with a Teflon® mixing tip. Before homogenization, stomach contents, beaks, feathers and feet were removed from the young birds, and the samples reweighed. After homogenization samples were split and stored in solvent-rinsed glass containers. One portion was sent to Michigan State University for the H4IIE bioassay (Jones *et al.* 1993), while the remainder was retained at the Duluth U.S. Environmental Protection Agency (EPA) laboratory for chemical analyses.

A brief description of the instrumental analysis is presented here; detailed descriptions of the methods and specific quality assurance and quality control procedures for the PCB, PCDF, and PCDD analyses are given elsewhere (U.S. Environmental Protection Agency 1990a, 1990b; Kuehl *et al.* 1991). Tissue samples (generally 20 g) were blended with 80 g of sodium sulfate. The mixture then was packed into a soxhlet thimble and spiked with recovery standards. For PCDDs and PCDFs, the recovery standards were C^{13}-labeled 2,3,7,8-substituted compounds, one for each homologue series, except in two cases where the C^{13}-labeled heptachlorodibenzo-*p*-dioxin was used for the heptachlorodibenzofuran and the C^{13}-labeled octachlorodibenzo-*p*-dioxin was used for the octachlorodibenzofuran. Similarly, C^{13}-labeled PCB congeners[3] 77, 126, and 169 were used as recovery standards for the planar PCBs. PCB congeners 14, 65, and 166 were employed as recovery standards for the nonplanar PCBs.

The spiked samples were extracted overnight with 300 ml of 1:1 (v/v) pesticide grade hexane/methylene chloride. The extract was reduced to a constant volume at 85°C in a Kuderna-Danish concentrator fitted with a Snyder column. The quantity of lipid present in the extract was determined gravimetrically. The extract was transferred in hexane to a column of acid Celite (10 g Baker Celite 545, 5 ml concentrated sulfuric acid) and potassium silicate (2 g on the bottom, separated from the acid Celite by sodium sulfate). The celite column was eluted with 100 ml of hexane. After reduction to approximately 1 ml, with isooctane as a keeper, the extract was transferred to a carbon column that consisted of approximately 0.2 g of a mixture 20:1 (w/w) of silica gel and Amoco PX-21 carbon in a disposable Pasteur pipette. The carbon column was first eluted with 20 ml of hexane (this defined the "forward" direction); this fraction contained predominantly nonplanar

[3]The IUPAC numbering system for the PCB congeners is used throughout: 3,5-dichlorobiphenyl, PCB 14; 2,4,6-trichlorobiphenyl, PCB 30; 2,3,5,6-tetrachlorobiphenyl, PCB 65; 3,3',4,4'-tetrachlorobiphenyl, PCB 77; 2,3,3'4,4'-pentachlorobiphenyl, PCB 105; 3,3',4,4',5-pentachlorobiphenyl, PCB 126; 2,3,4,4',5,6-hexachlorobiphenyl, PCB 166; 3,3',4,4',5,5'-hexachlorobiphenyl, PCB 169; 2,2',3,4,4',5,6,6'-octachlorobiphenyl, PCB 204.

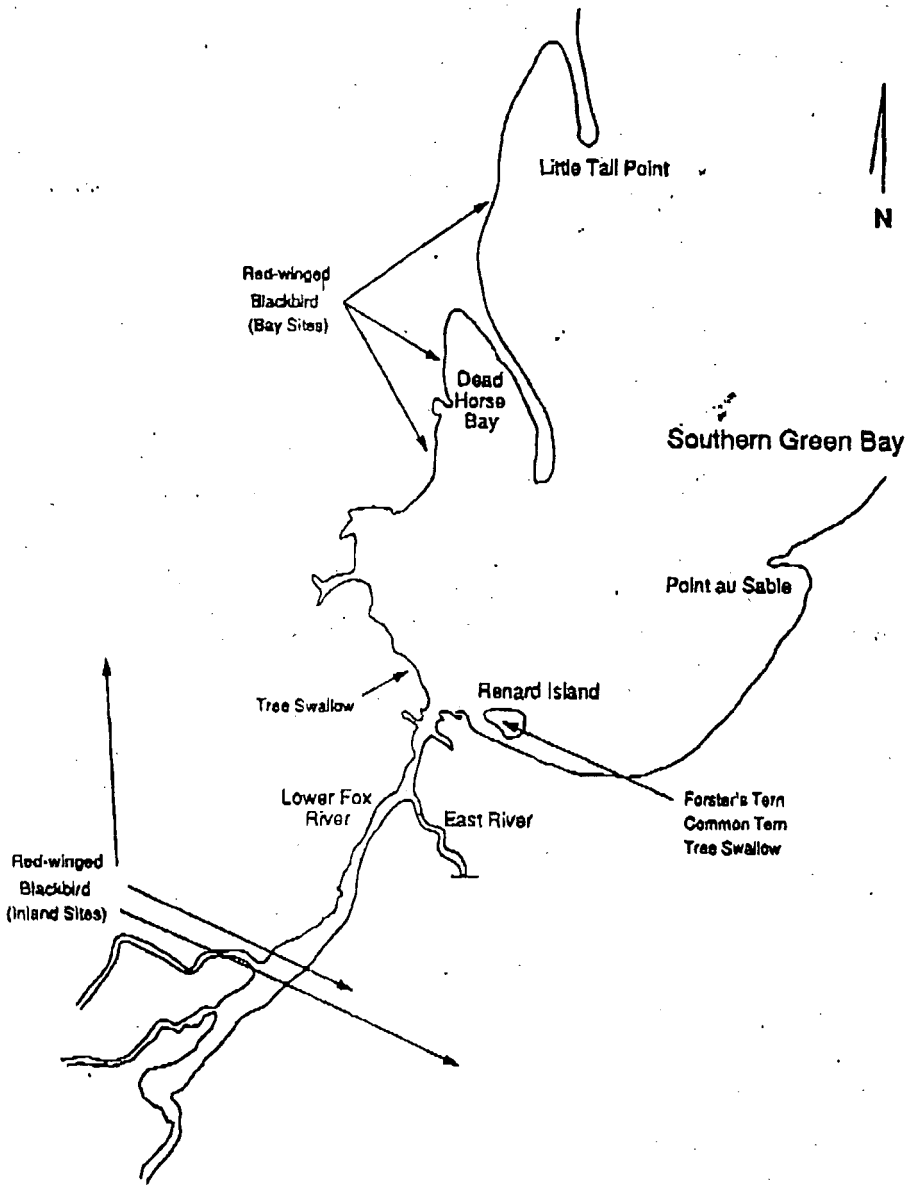

Fig. 1. Sampling sites for Forster's tern, common tern, tree swallows, and red-winged blackbirds along the lower Fox River/Green Bay, Wisconsin

PCBs. The carbon column was then eluted with 25 ml of 1:1 (v/v) benzene/methylene chloride in the forward direction; this fraction contained predominantly planar PCBs including the non ortho-substituted congeners 77, 126, and 169, and mono ortho-substituted congeners such as 105. The carbon column was finally eluted in the reverse direction with 21 mL of toluene to obtain a fraction containing PCDDs and PCDFs. Toluene was added to the planar PCB fraction, and both the planar PCB and PCDF/PCDD fractions were reduced to 100 µl. Isooctane was added to the nonplanar PCB fraction, which then was reduced to 1 ml.

Fractions containing the PCDDs, PCDFs and planar PCBs were subjected to gas chromatographic separation using a 30-m DB-5 capillary column, and were quantified with a Finnigan-MAT 8230 double-focusing mass spectrometer. Calibration provided the relative response factor of the native analytes and C^{13}-labeled congeners (recovery standards) within each homologue series, from which concentrations of the analytes were calculated. Extraction efficiencies (recoveries) were measured using the relative responses of internal reference (added to extracts before gas chromatography) and recovery standards. Selective ion monitoring provided for confirmation of certain analytes (*i.e.*, 2,3,7,8-substituted PCDDs and PCDFs, and PCB congeners 77, 126, and 169) by comparing relative retention times of native to the corresponding C^{13}-labeled ions. Ratios of signals for two principal ions (ion ratios) also were used for confirmation. PCB 105 (for which no C^{13}-labeled isomer was available at the time of this study) was quantified by comparison to the recovery of C^{13}-labeled PCB 126; therefore, estimates of concentrations of PCB 105 in the samples may be low because a certain quantity of this congener could elute in the nonplanar PCB fraction (P. Cook, U.S. EPA, Duluth, pers. comm.).

For the nonplanar PCBs, quantifications were performed with a Hewlett-Packard 5710 gas chromatograph equipped with a 30-m DB-5 capillary column and an electron capture detector. Before chromato-

graphic analysis, two internal standards, PCB congeners 30 and 204, were added to all samples. Quantifications against an internal standard were performed on each sample and response factors for each chromatographic component determined by analyzing a mixture of Aroclors® 1232, 1248, and 1262 [25:18:18 (U.S. Environmental Protection Agency, 1988)]. Total concentrations of PCBs were calculated by summing the concentrations of the individual congeners.

Samples for the H4IIE bioassay were extracted after the method of Ribick et al. (1981) as modified by Tillitt *et al.* (1991a). General procedures and calculations used for the H4IIE bioassays are described in detail elsewhere (Ankley *et al.* 1991; Tillitt *et al.* 1991a, 1991b; Jones *et al.* 1993).

A total of 48 egg and chick samples were evaluated using the H4IIE bioassay, while a subset of 25 of these samples was analyzed for PCBs, PCDFs, and PCDDs. For a number of reasons, the Forster's tern sample set received the most attention. First, there was adequate sample mass for all analyses. Second, the Forster's tern samples provided the most nearly complete data in terms of evaluating contaminant uptake over time. Finally, there was a historical database of PCB, PCDF, and PCDD residue concentrations for this particular Forster's tern colony, and a suspicion that these classes of compounds were responsible for reproductive impairment in the birds in a 1983 study (Kubiak *et al.* 1989). [Harris *et al.* (1993) provide a detailed comparison of the biological and chemical results from the present study with those of Hoffman *et al.* (1987) and Kubiak *et al.* (1989).]

To account for growth dilution when assessing uptake of contaminants by the birds, PCB, PCDF, PCDD, and TCDD-EQ concentrations were multipled by the initial sample weight (eggs) or trimmed sample weight (chicks or nestlings) to express the variables on a total mass basis. When samples had been pooled, the mean weight of the eggs or chicks constituting the sample was used for these data manipulations. Accumulation of the PCHs and TCDD-EQ was evaluated by comparing the total mass of contaminants present in the chicks or nestlings to the total mass of contaminants present in the eggs. In the case of the tern samples, this was done on a nest-by-nest basis, that is, the mass of contaminant present in the egg was subtracted from the mass present in the chick from the same nest. Because studies have shown that among-nest variation in concentrations of contaminants in birds is greater than within-nest variation (Becker *et al.* 1989; Custer *et al.* 1990), it was felt that this approach was more appropriate than to use a colony mean value for contaminant mass in the eggs. For the red-winged blackbird and tree swallow samples this approach could not be used, as the eggs had to be pooled for the residue and bioassay analyses.

Uptake data were analyzed using MINITAB® (Ryan *et al.* 1985). Data initially were tested and verified for normality using normal probability plots. The null hypothesis, that there was no significant uptake of PCBs, PCDFs, PCDDs and/or TCDD-EQ, was evaluated for Forster's terns by using *t*-tests to compare the total mass of contaminants in eggs to total mass in the chicks. We then calculated uptake rates for the PCBs, PCDFs, PCDDs, and TCDD-EQ by the Forster's tern chicks by regressing chick age versus total contaminant mass present in the chicks (minus the mass present in eggs from the same nests). When the contaminant mass in the egg was greater than in the chick (as was the case for the 3-day-old Forster's tern; see Table 1), a value of zero was assigned for the regression analysis. The uptake rate was defined as the slope of statistically significant linear relationships between age and contaminant mass. Sample sizes were too small to permit a comparable statistical evaluation of the uptake of PCHs in the other three test species; however, there were adequate numbers of samples to utilize analysis of variance to evaluate among-species variation in TCDD-EQ concentrations.

For data evaluation by principal components analysis (PCA) and classification, we used SIMCA-3B (Soft Independent Modeling of Class Analogy; Principal Data Components, Columbia, Missouri). For computational purposes, concentrations which were less than the limit of quantification (LOQ) or detection (LOD) were assumed to be one-half the LOQ or LOD (De Vault *et al.* 1989). Other combinations of quantification or detection limits, such as using zero or the limit itself, had only a minor affect on PCA results and interpretation. Lipid-normalized concentrations of contaminants were used for the PCA. However, because the uptake analysis was based upon total mass of the contaminants in the various samples, it was not necessary to use lipid-normalized data before statistical manipulations. Results of all comparisons were considered significant at $p \leq 0.05$.

Results and Discussion

PCH Concentrations

Several of the 2,3,7,8-substituted PCDFs and PCDDs were not quantifiable or not detectable in eggs or young from the four species (Tables 1 and 2). Concentrations of total PCBs, PCB congeners 77, 105, 126 and 169, TCDD, and 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD) were detectable in all the Forster's tern samples, and 2,3,7,8-tetrachlorodibenzofuran (TCDF), 1,2,3,6,7,8-hexachlorodibenzofuran (HxCDF), 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF), 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PeCDD), 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), and octachlorodibenzo-*p*-dioxin (OCDD) usually were detectable (Table 1). These same PCB, PCDF, and PCDD congeners also generally were present in the common tern samples (Table 2). Total concentrations of PCBs and PCB congeners 77 and 105 were quantifiable in all of the red-winged blackbird samples (Table 2). PCB congeners 126 and 169, as well as TCDF, HxCDF, HpCDF, TCDD, and OCDD were not quantifiable or not detectable in several of the red-winged blackbird nestling and egg samples. Total PCBs, PCB congeners 77, 105, 126 and 169, TCDF, TCDD, HxCDD, and HpCDD were quantifiable in all the tree swallow samples (Table 2). Unlike the other birds, the tree swallows consistently contained quantifiable concentrations of 1,2,3,7,8-pentachlorodibenzofuran and 1,2,3,4,7,8-hexachlorodibenzofuran; moreover, concentrations of TCDF in the tree swallow samples were greater than in the other species (Table 2).

With the exception of TCDF, the general trend of concentrations of PCBs, PCDFs, and PCDDs from greatest to least was Forster's tern ~ common tern > tree swallow > red-winged blackbird. The similarity in concentrations of PCHs between the two tern species was expected given their similar life histories and the close proximity of the two colonies. The greater PCH concentrations in the tree swallows than in the red-winged blackbirds was somewhat unexpected given the presumed similarity in diet between the two species. In addition, the tree swallows colonizing the nest boxes likely were first year females that had not previously been exposed to the lower Fox River and Green Bay system. In contrast, at least some of the red-winged blackbirds likely had inhabited the associated wetlands in previous years. It is possible, however, that red-winged blackbirds foraged more on relatively uncontaminated upland food sources than did the tree swallows, which may have gained their food primarily from insects (presumably chironomids) emerging in the river and bay (pers. obs. of G.J.N.; Quinney and Ankney 1985). Part of the difference in residue concentrations between the species also may be related to the fact that the tree swallows had about twice as much lipid as the red-winged blackbirds.

Table 1. Concentrations of total PCBs, PCB congener 77, 105, 126 and 169, and 2,3,7,8-substituted PCDDs and PCDFs in eggs and chicks from a Forster's tern colony on a CDF in the lower Fox River/Green Bay watershed. Total PCBs are in ng/g, while other concentrations are in pg/g. PCB congeners are given by IUPAC numbers, while substitution patterns are used to indicate PCDDs and PCDFs. Also indicated [illegible] sample [illegible] lipid and weight. To obtain the total contaminant masses described in the text, multiply sample weight by the contaminant concentration of interest. Sample identification numbers are indicated in parentheses

Sample				PCBs				PCDDs		PCDFs														
(Sample [illegible])	[illegible] (g)	[illegible] (g)	PCBs	77	105	126	169	2378	[illegible]	12347	23678	123789	34678	678	2378	123	23678	123678	678	234678	123789	678	1234789	OCDF
Egg Nest 1 (1)	10.9	18.19	7380	7320	233000	2260	160.0	10.6	[illegible]	[illegible]	14.7	<2.8[a]	8.8	133.0	<0.9	<ND(5.3)[b]	<NQ(5.6)[c]	<0.4	<0.9	<NQ(9.1)	ND(9.1)	1.5	ND(17.4)	ND(60.0)
Chick, [illegible] Nest 1 (2)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	36.0	[illegible]	[illegible]	NQ([illegible])	[illegible]	[illegible]	[illegible]	NQ([illegible])	[illegible]	<NQ([illegible])	<NQ([illegible])	<NQ([illegible])	<0.3	<ND(2.8)	ND(2.8)	ND(5.3)	ND(18.4)	ND(18.4)
Egg Nest 3 (3)	10.6	17.22	6400	5070	225000	1690	62.2	4.6	4.1	ND(5.6)	8.0	<NQ(5.6)	7.7	135.0	<NQ(1.8)	<NQ(5.6)	<NQ(5.6)	<NQ(9.2)	<0.6	<1.0	ND(9.2)	2.7	ND(17.7)	ND(60.9)
Chick, 15 d Nest 3 (4)	9.3	18.46	3890	7850	84800	1120	24.8	2.0	2.4	0.9	5.1	<NQ(1.7)	4.9	8.4	<1.0	<NQ(1.7)	<0.5	<NQ(2.7)	<0.3	<ND(2.7)	ND(2.7)	1.5	ND(5.2)	ND(18.1)
Egg Nest 4 (5)	11.6	21.09	5400	5610	275000	2000	90.0	6.1	4.9	NQ(4.2)	8.4	<1.1	6.3	82.4	<NQ(1.7)	<ND(4.2)	<0.6	<NQ(6.9)	<NQ(6.9)	<NQ(7.1)	ND(6.9)	2.7	ND(13.2)	ND(45.7)
Chick, 20 d Nest 4 (6)	15.9	114.9	4090	13200	74500	1260	34.5	2.3	3.4	NQ(2.7)	7.4	<0.7	10.6	26.6	<1.6	<0.2	<NQ(2.1)	<1.2	<NQ(2.9)	<ND(2.8)	ND(2.8)	9.0	ND(5.3)	ND(39.0)
Chick, 27 d Nest 4 (7)	10.4	109.4	5070	6890	115000	1550	44.3	3.0	3.4	0.7	6.0	<NQ(1.7)	4.3	6.1	<0.3	<ND(1.7)	<0.4	<NQ(2.8)	<0.4	<ND(2.8)	ND(2.8)	1.3	ND(5.3)	ND(18.3)
Chick, 27 d Nest 4 (8) (Duplicate)	13.5	—	4180	6850	87100	1500	48.8	3.0	3.1	1.1	6.0	<NQ(1.7)	4.5	6.0	<NQ(0.7)	<ND(1.7)	<NQ(1.8)	<0.2	<0.4	<ND(2.8)	ND(2.8)	1.3	ND(5.3)	ND(18.4)
Egg Nest 5 (9)	13.5	17.73	7970	3760	414000	2670	167.0	20.4	5.0	NQ(6.8)	9.6	<NQ(6.8)	6.3	114.0	<0.7	<ND(6.7)	<0.8	<NQ(11.1)	<0.8	<ND(11.1)	ND(11.1)	NQ(21.6)	ND(21.2)	ND(73.1)
Chick, 26 d Nest 5 (10)	5.7	106.0	3640	1660	107000	2060	50.5	3.6	1.9	0.7	5.5	<NQ(1.7)	5.2	9.8	<0.1	<0.1	<0.1	<NQ(2.8)	<0.4	<ND(2.8)	ND(2.8)	2.0	ND(5.3)	2.9
Egg Nest 6 (11)	11.3	17.62	9520	5080	340000	3320	154.0	10.7	8.5	0.8	16.2	<NQ(6.8)	7.8	163.0	<NQ(2.2)	<ND(6.7)	<NQ(7.0)	<0.5	<1.4	<0.9	ND(11.1)	3.4	ND(21.2)	ND(73.1)
Chick, 3 d Nest 6 (12)	5.3	24.43	4150	1590	179000	1370	80.4	3.6	NQ(9.7)	NQ(4.9)	6.3	<NQ(4.9)	4.2	16.9	<NQ(1.4)	<ND(4.8)	<ND(4.8)	<NQ(7.9)	<0.7	<ND(9.2)	ND(7.9)	9.0	ND(15.2)	ND(32.5)
Chick, 13 d Nest 6 (13)	11.7	15.95	3970	7620	79600	1180	30.0	3.1	2.2	NQ(2.1)	4.8	<NQ(1.7)	5.2	8.7	<1.1	<0.1	<NQ(2.0)	<NQ(2.8)	<0.4	<ND(2.8)	ND(2.8)	1.6	ND(5.3)	ND(18.3)

[a] In cases where coelution occurs, data for the 2,3,7,8-substituted isomer are quoted as "<" a certain value. On the DB5 column, 123789 PCDD coelutes with 123467 PCDD. Also on the DB5 column, 2378 PCDF coelutes with 1279, 1249, 1246, 2346, 2347, and 2348 PCDF; 2467 coelutes with 1269 and 1239; 12378 coelutes with 12348; 23478 coelutes with 12369, 13489 and 12489; 123478 coelutes with 123467; 123678 coelutes with 123479; and 234678 with 123689

[b] ND(#), not detectable (detection limit)

[c] NQ(#), not quantifiable (quantification limit)

Table 2. Concentrations of total PCBs, PCB congeners 77, 105, 126 and 169, and 2,3,7,8-substituted PCDDs and PCDFs in eggs and young of common terns, red-winged blackbirds, and tree swallows nesting in the lower Fox River/Green Bay watershed. Total PCBs are in ng/g, while other concentrations are in pg/g. PCB congeners are given by IUPAC numbers, while substitution patterns are used to indicate PCDDs and PCDFs. Also indicated for each sample are percent lipid and weight. For pooled samples the mean weight of the eggs or young comprising the sample is indicated. To obtain the total contaminant masses described in the text, multiply sample weight by the contaminant concentration of interest. Sample identification numbers are indicated in parentheses

Species	Sample type (identification)	Percent lipid	Sample wt. (g)	Total PCB	PCBs 77	105	126	169	PCDDs 2378	12378	123478	123678	123789	1234678	OCDD	PCDFs 2378	12378	23478	123478	123678	234678	123789	1234678	1234789	OCDF
Common tern	Egg Nest 3(14)	[illegible]	[illegible]	[illegible]	30700	[illegible]	[illegible]	[illegible]	10.6	NQ(22.[illegible])	[illegible]	19.2	<NQ(8.4)	12.[illegible]	[illegible]	<11.0[a]	<1.4	<7.5	<NQ(13.7)	<2.8	<11.1	ND(13.7)[c]	36.4	ND(36.2)	ND(90.5)
Common tern	Chick, 3-4 Nest 3(15)	6.6	36.21	[illegible]	[illegible]	22600	2370	131.0	<.7	4.1	0.7	3.9	<NQ(2.8)	4.1	11.0	<4.2	<0.2	<NQ(3.1)	<NQ(4.6)	<NQ(4.6)	<1.1	ND(4.6)	3.0	ND(8.8)	NQ(30.7)
Common tern	Chick, 3-4 Nest 3(16) (Duplicate)	6.3	—	[illegible]	[illegible]	24300	2400	142.0	5.1	4.4	NQ(3.4)	6.7	<NQ(3.6)	4.7	12.1	<5.3	<NQ(3.4)	<0.8	<NQ(5.5)	<0.7	<NQ(5.5)	ND(5.5)	3.6	ND(10.5)	ND(36.3)
Common tern	Egg Nest 4(17)	11.2	17.30	[illegible]	19100	>398000	2430	24.[illegible]	5.6	7.6	[illegible]	10.2	<NQ(6.7)	[illegible]	[illegible]	<10.6	<1.0	[illegible]	<NQ(11.0)	<NQ(11.0)	[illegible]	ND(11.0)	3.2	ND(11.7)	ND(72.5)
Common tern	Chick, 16-4 Nest 4(18)	7.3	77.22	[illegible]	23200	91800	1440	51.0	2.5	3.0	1.2	7.8	<NQ(1.7)	9.0	18.0	<4.0	<NQ(1.7)	<4.9	<0.3	<0.4	<0.6	ND(2.8)	NQ(8.4)	ND(5.3)	ND(18.3)
Red-winged blackbird	Egg[e] Island 1(19)	8.9	2.99	340	15.9	1050	11.6	ND(3.0)	NQ(1.9)	1.2	0.3	2.2	<NQ(4.6)	3.[illegible]	1.7	<0.3	<ND(4.8)	<ND(2.4)	<ND(7.[illegible])	<ND(7.9)	<ND(1.[illegible])	ND(7.1)	ND(15.1)	ND(52.[illegible])
Red-winged blackbird	Egg Island 1(20) (Duplicate)	8.6	—	350	17.9	1030	NQ(13.0)	NQ(3.0)	0.2	0.9	NQ(4.8)	2.0	<NQ(4.8)	3.4	10.7	<ND(1.4)	<ND(4.8)	<ND(4.8)	<ND(7.9)	<ND(7.9)	<ND(7.9)	ND(7.9)	ND(15.1)	ND(15.1)	ND(52.0)
Red-winged blackbird	Nestling Island 1(21)	5.4	26.32	53	126	1480	10.8	ND(2.0)	ND(1.4)	ND(2.6)	NQ(3.4)	0.2	<ND(3.4)	NQ(2.7)	NQ(27.6)	<ND(1.0)	<ND(3.4)	<ND(3.4)	<ND(5.5)	<ND(5.5)	<ND(5.5)	ND(5.5)	ND(10.6)	ND(10.6)	ND(36.6)
Red-winged blackbird	Egg[e] Bay 2(22)	7.3	2.03	1080	492	22900	89.3	16.0	0.4	NQ(4.3)	1.2	NQ(8.1)	<ND(4.2)	4.2	29.0	<1.1	<NQ(4.2)	<NQ(4.2)	<ND(6.9)	<ND(6.9)	<ND(6.9)	ND(6.9)	ND(13.2)	ND(13.2)	ND(45.4)
Red-winged blackbird	Nestling Bay 2(23)	5.4	28.08	705	1290	26300	154	3.5	0.6	2.0	2.2	7.4	<ND(3.4)	9.0	8.4	<3.1	<NQ(3.4)	<0.2	<0.1	<ND(5.6)	<ND(5.6)	NQ(5.6)	0.7	ND(10.7)	ND(36.9)
Red-winged blackbird	Egg[f] Bay 3(24)	6.8	2.49	1180	1130	27800	161	11.8	0.5	2.6	2.1	6.9	<ND(4.8)	8.5	20.4	<3.1	<0.2	<0.7	<NQ(7.9)	<ND(7.9)	<NQ(7.9)	<NQ(7.9)	1.0	ND(15.1)	ND(52.2)
Red-winged blackbird	Nestling Bay 3(25)	6.6	32.48	780	965	24100	230	5.5	0.7	3.5	NQ(5.8)	10.3	<ND(2.9)	NQ(10.8)	111.0	<3.6	<NQ(2.9)	<0.4	<ND(4.7)	<ND(4.7)	<ND(4.7)	ND(4.7)	6.2	ND(9.0)	NQ(173.0)
Tree swallow	Egg[g] River(26)	10.8	1.23	4120	42500	116000	1050	78.7	5.2	24.1	23.7	101.0	<NQ(7.3)	109.0	140.0	<39.9	<5.2	<6.5	<2.7[i]	<2.3	<0.8	ND(7.9)	NQ(29.6)	ND(15.1)	ND(52.2)
Tree swallow	Nestling, 16-d[h] River(27)	13.1	16.76	2490	41200	47200	752	18.0	2.3	8.2	10.7	39.4	<2.3	56.0	22.[illegible]	<26.4	<2.4	<2.1	<1.1	<1.3	<NQ(2.8)	ND(2.8)	5.2	ND(5.3)	ND(18.3)
Tree swallow	Nestling[i] CDF(28)	11.3	16.05	2970	22500	66500	1180	54.0	2.8	NQ(11.7)	12.2	48.4	<NQ(3.3)	71.4	NQ(24.9)	<23.7	<2.3	<NQ(3.6)	<0.8	<NQ(3.6)	<ND(2.8)	ND(2.8)	6.1	ND(5.3)	ND(18.3)

[a] NQ(#), not quantifiable (quantification limit)
[b] In cases where coelution occurs, data for the 2,3,7,8-substituted isomer are quoted as "<" a certain value. On the DB5 column, 123789 PCDD coelutes with 123467 PCDD. Also on the DB5 column, 2378 PCDF coelutes with 1279, 1249, 1246, 2346, 2347, and 2348 PCDF; 3467 coelutes with 1269 and 1239; 12378 coelutes with 12348; 23478 coelutes with 12369, 13489 and 12489; 123478 coelutes with 123467; 123678 coelutes with 123479; and 234678 coelutes with 123689
[c] ND(#), not detectable (detection limit)
[d] Composite of 10 eggs
[e] Composite of 8 eggs
[f] Composite of 9 eggs
[g] Composite of 19 eggs
[h] Composite of 4 nestlings
[i] Composite of 3 nestlings

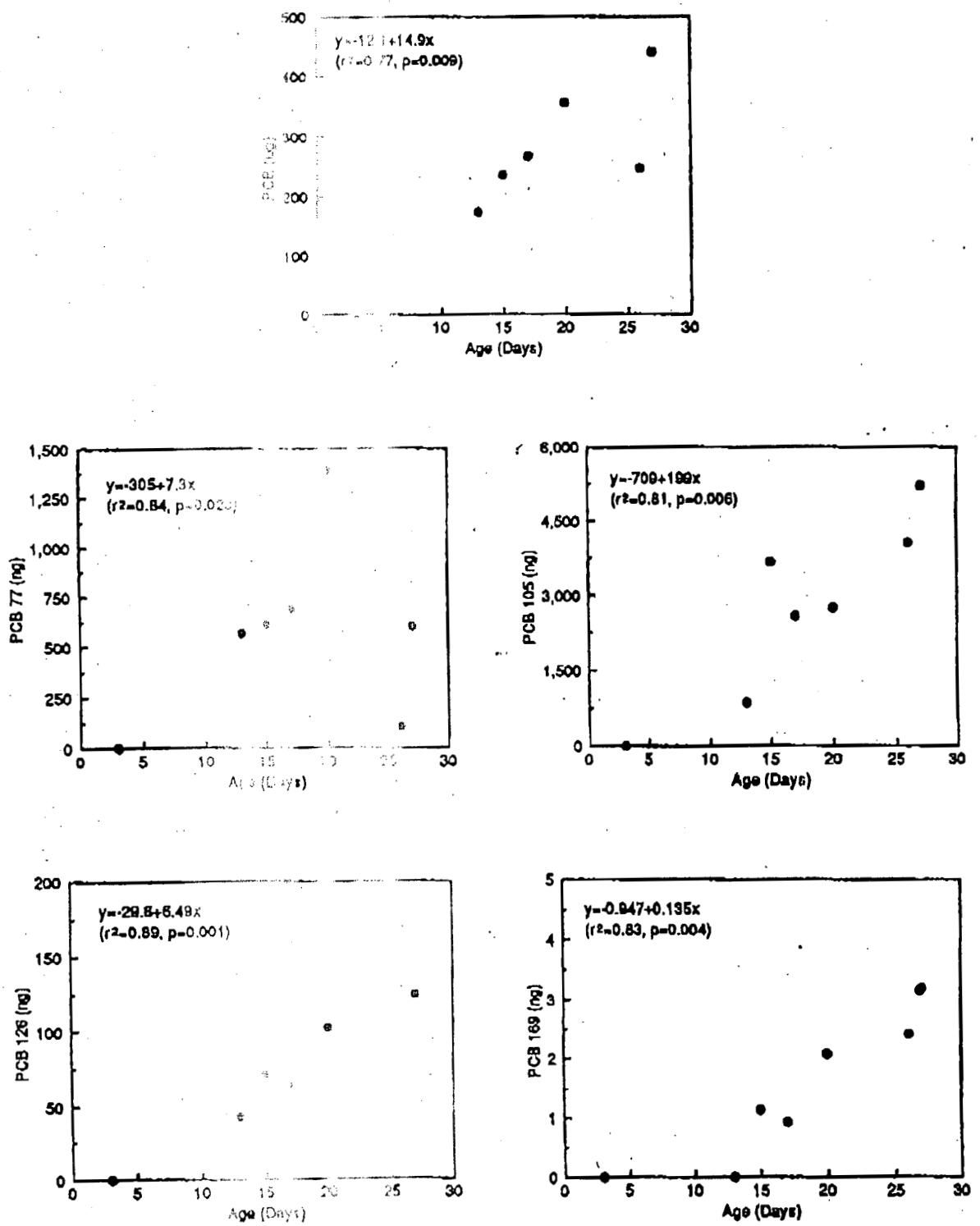

Fig. 2. Accumulation of total PCBs and PCB congeners 77, 105, 126, and 169 by Forster's tern chicks nesting on a CDF in the lower Fox River. The indicated regression equation for congener 77 excluded the data points for the 26- and 27-day-old chicks

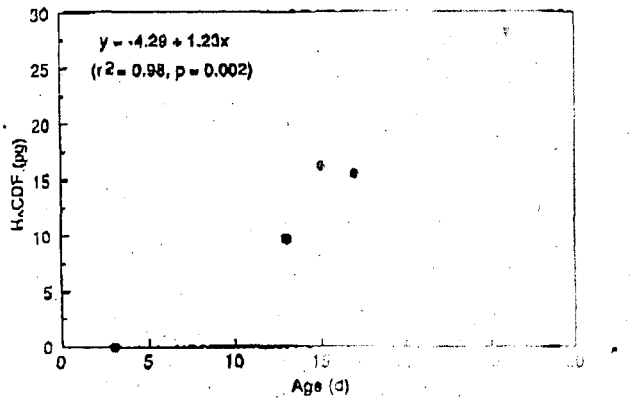

Fig. 3. Accumulation of HxCDF by Forster's tern chicks nesting on a CDF in the lower Fox River

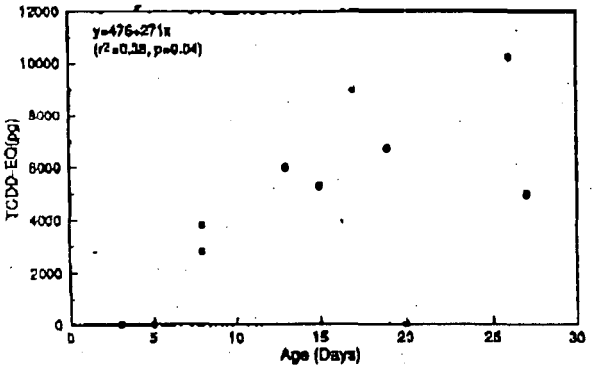

Fig. 4. Accumulation of TCDD-EQ by Forster's tern chicks nesting on a CDF in the lower Fox River

PCH Accumulation Rates

Evaluation of the total mass of contamin[illegible] accu[illegible]ulated by the Forster's tern chicks was conducted for th[illegible]e PC[illegible], PCDF, and PCDD congeners which were usually [illegible]ent at quantifiable concentrations in both the egg and chick [illegible]mples. There were significantly greater masses of total [illegible] PCB congeners 77, 105, 126, HxCDF, PeCDD, HxCD[illegible], [illegible] HpCDD in chicks than in eggs from the same nest (Tab[illegible]). In th[illegible] case of PCB congener 169, the total mass in the [illegible] was appr[illegible]ximately 60% greater than in the eggs; howev[illegible] dif[illegible] was not statistically significant (p = 0.0[illegible]). [illegible]tion [illegible] of contaminants by the Forster's tern chic[illegible] [illegible]ever [illegible] significant linear models for total PCBs, PCB [illegible]ers [illegible] and 169, and HxCDF (Figures 2 and 3). Th[illegible] uptake [illegible] for total PCBs was approximately 15 µg/d[illegible] [illegible] uptake rates for PCB congeners 105, 126, 169 and [illegible] about [illegible], 6.5, 0.14, and 0.001 ng/day, resp[illegible] [illegible] 3). There was a linear rate of upt[illegible] 77 for approximately 20 days; howeve[illegible] was a substantial decrease in the total [illegible] 26- and 27-day-old Forster's tern ch[illegible] [illegible] explanation for this observation [illegible] of the [illegible] of the chicks to efficiently metabolize [illegible] In general, PCB congeners with a les[illegible] more readily metabolized and ex[illegible] congeners. The accumulation of [illegible] Forster's tern chicks resulted in [illegible] model with an uptake rate of ab[illegible]).

Although there was significan[illegible] of the PCDD congeners (PeCD[illegible] the Forster's tern chicks, this incre[illegible] able using a linear model with ag[illegible] variable. The lack of a linear uptake for [illegible] related to the possible onset of [illegible] in the chicks, as may have been the [illegible] 77. Further research is required to d[illegible] influence the bioaccumulation of [illegible]s.

Sample sizes were too sma[illegible] analysis of PCH uptake in com[illegible] blackbird and tree swallow nestlings; however, there was a clear and consistent pattern of PCH uptake by young of all three species (Table 2). Uptake based on total contaminant mass (*i.e.*, concentration × sample weight) was pronounced for total PCBs and PCB congeners 77, 105, 126, and, occasionally, 169. Contaminant concentrations and total masses in eggs and nestlings tended to be higher in red-winged blackbirds from the bay sites than from the inland site (Table 2), a result consistent with the pattern recognition analysis described below. Contaminant concentrations and masses in tree swallow nestlings were similar in samples from the river and CDF sites (Table 2).

There were detectable concentrations of TCDD-EQ in all samples of eggs and young from the four test species (Jones *et al.* 1993). There were significant among-species variations in TCDD-EQ in both eggs and chicks. The Forster's and common terns had the greatest concentrations of TCDD-EQ, the tree swallows lesser concentrations, and red-winged blackbirds the smallest concentrations. As was the case for several of the PCHs, the mass of TCDD-EQ in the Forster's tern chick samples was significantly greater than in the eggs. Also, the regression model of TCDD-EQ mass versus age in the Forster's tern chick samples (minus mass in the eggs) was significant, with an uptake rate of approximately 270 pg/day (Figure 4). That trends in TCDD-EQ in the four species were similar to those observed for the PCHs was not surprising, given the strong positive correlations noted by Jones *et al.* (1993) between TCDD-EQ concentrations and concentrations of PCBs and PCB congeners in these same test samples.

We observed a curious trend in the concentration of PCBs and PCDDs in the Forster's and common tern samples. Both the 3-day-old Forster's tern chick (sample 12; Table 1) and the 5-day-old common tern chick (sample 15; Table 2) had smaller masses of many of the PCHs than the corresponding sibling eggs. This same phenomenon was noted by Scharenberg (1991), who also compared contaminant concentrations in tern eggs to concentrations in young chicks. He hypothesized that the effect could result from either onset of the ability of the chicks to metabolize and excrete organic contaminants upon hatching, or incomplete transfer of all contaminants in egg contents to the newly hatched chicks. Further studies are necessary to distinguish between those hypotheses.

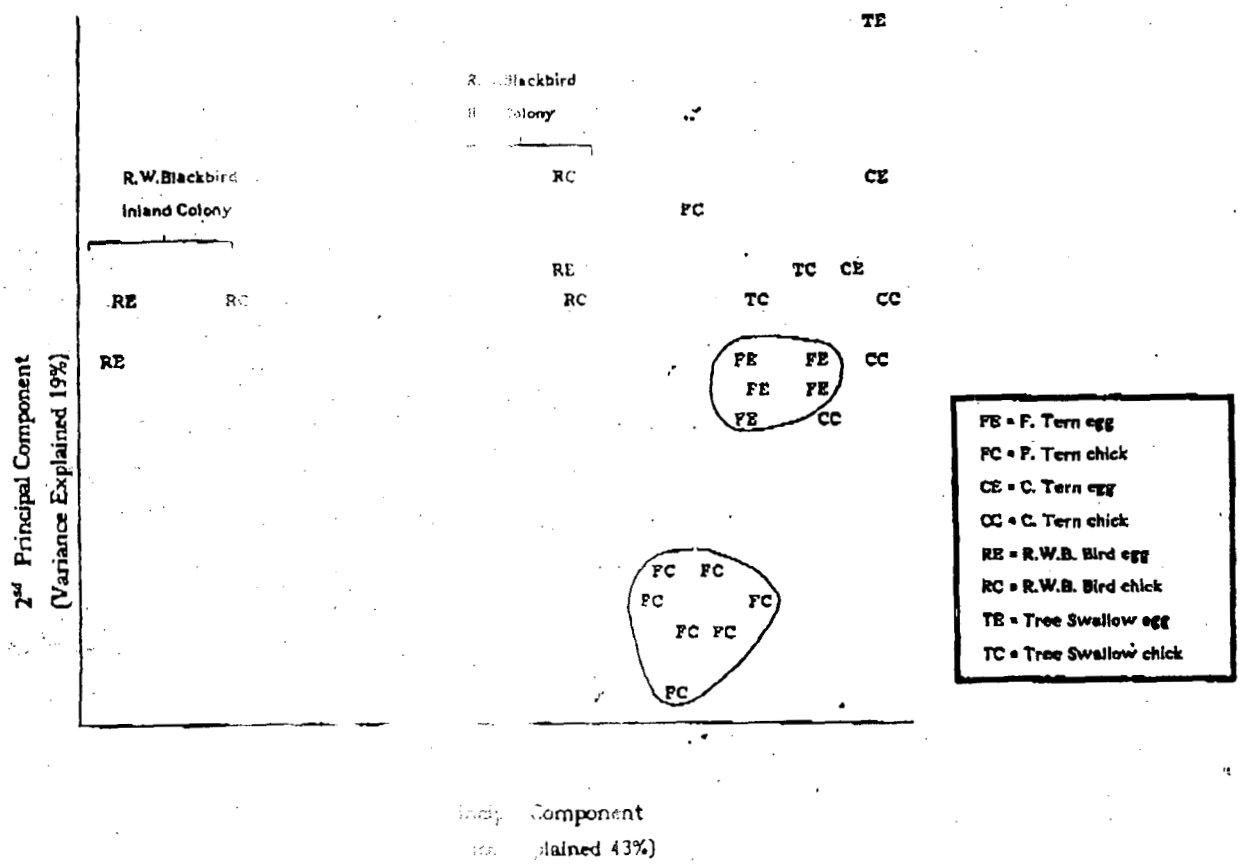

Fig. 5. Plot of the first two prin[illegible] CDD, and PCDF data from bird eggs and young

Multivariate Analysis

To further evaluate chem[illegible] lue p[illegible] the test species, we applied PCA [illegible] the [illegible] atterns. All concentration data w[illegible] -tran[illegible] ce the influence of unusually l[illegible] ntr[illegible] s in the different sample matrices [illegible] d et al. 1984). After lipid-normalizati[illegible] log[illegible] a, a PCA was calculated on the 28 samples [illegible] DF, and PCDD congeners measured in t[illegible] sa[illegible] rst three principal components (PC) a[illegible] d for [illegible] ariability in the original 21 variabl[illegible] valid [illegible] used to determine that all three p[illegible] mpo[illegible] ically significant (Wold 1978, [illegible] ject[illegible] mples for the first two PC and [illegible] points give a graphical image [illegible] in the samples (Figure 5). Data [illegible] of the chemical analyses are reflect[illegible] of each replicate analysis of a Forste[illegible] ter chic[illegible] nd 8), a common tern chick (samp[illegible] -winged blackbird egg sample fro[illegible] nd 20).

Chemical concentratio[illegible] tree swallows, red-winged bl[illegible] terns, and common terns form d[illegible] each other (Figure 5). The dist[illegible] and eggs in tree swallows, red-winged blackbirds, and common terns was difficult to quantitatively assess because sample sizes were limited. However, it is apparent that qualitative differences in the PCH profiles exist between chicks or nestlings and eggs of these species. The qualitative separations observed in the PCH profiles of young versus egg samples within a species may be a reflection of dietary exposure differences or may be related to differences in xenobiotic metabolism between the adults and young of a species. The most illustrative example of PCH profile differences based on geographical location is in the red-winged blackbird eggs and nestlings collected from two locations. One group, collected from one of the inland sites (samples 19–21) had a PCH profile that was markedly different from another group collected near the river (samples 22–25), which suggests that the two populations are exposed to different sources of PCHs. It is unlikely that metabolic differences would account for these different PCH profiles, however, the effect of differential exposure on metabolism cannot be ignored.

To determine which PCB, PCDF, and PCDD congeners were responsible for the clustering of samples in Figure 5, the 21 measured congeners were plotted in the same PC coordinate system as the samples (Figure 6). Positions of the chemicals in the coordinate system indicate the direction and magnitude that their presence has on the positions of the samples in Figure 5. For example, the four PCB congeners and TCDD in the lower

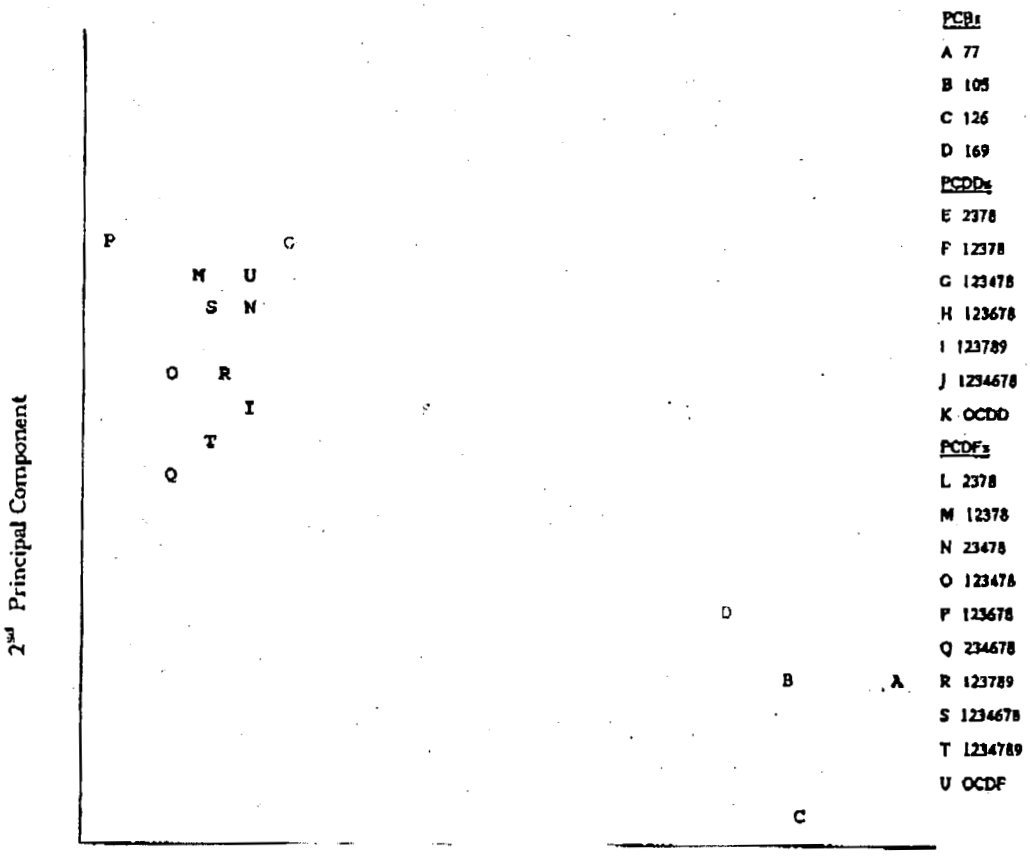

Fig. 6. Loading plot corresponding

right quadrant pulled samples
the lower right quadrant. Similarl
the y-axis was strongly influence

Forster's tern eggs and chicks
distinct groups (Figure 5); how
definition, residual or Coomans
1984; Vogt *et al.* 1987; Schw
Stalling 1991). In Coomans plo
separate class models are calc
axes. In these plots, the residu
onto different classes may be vis
interval is calculated from the
model by using an approximat
limits (Wold *et al.* 1984). The
was investigated by completing
ster's tern eggs and Forster's
based on two PCs and SIMCA
mine if the residue profiles in
cally different. Sample 12 was
analysis as an outlier (Figure
calculated, all samples were cl

the respective class model to determine if chemical profiles were statistically different. In the resulting classification plot (Figure 7) the area bound by the abscissa and the line parallel to abscissa-axis represents the 95% confidence level (*F*-test) for classification samples in the egg-model. The accuracy of the classification models was tested by withholding two samples (7 and 13) and reclassifying the remainder. The resulting classifications correctly assigned the withheld samples. Profiles of PCHs from eggs or young of common terns, tree swallow, and red-winged blackbirds indicate that they are not members of either Forster's tern egg- or chick-classes. This suggests either a difference in environmental exposure and/or metabolism of the PCB, PCDF and PCDD congeners in the four species.

Summary and Conclusions

This study indicates the importance of aquatic food chains in PCH transfer to avian species at different trophic levels in the lower Fox River and Green Bay ecosystem. There was a significant uptake of total PCBs and specific PCB, PCDF and PCDD

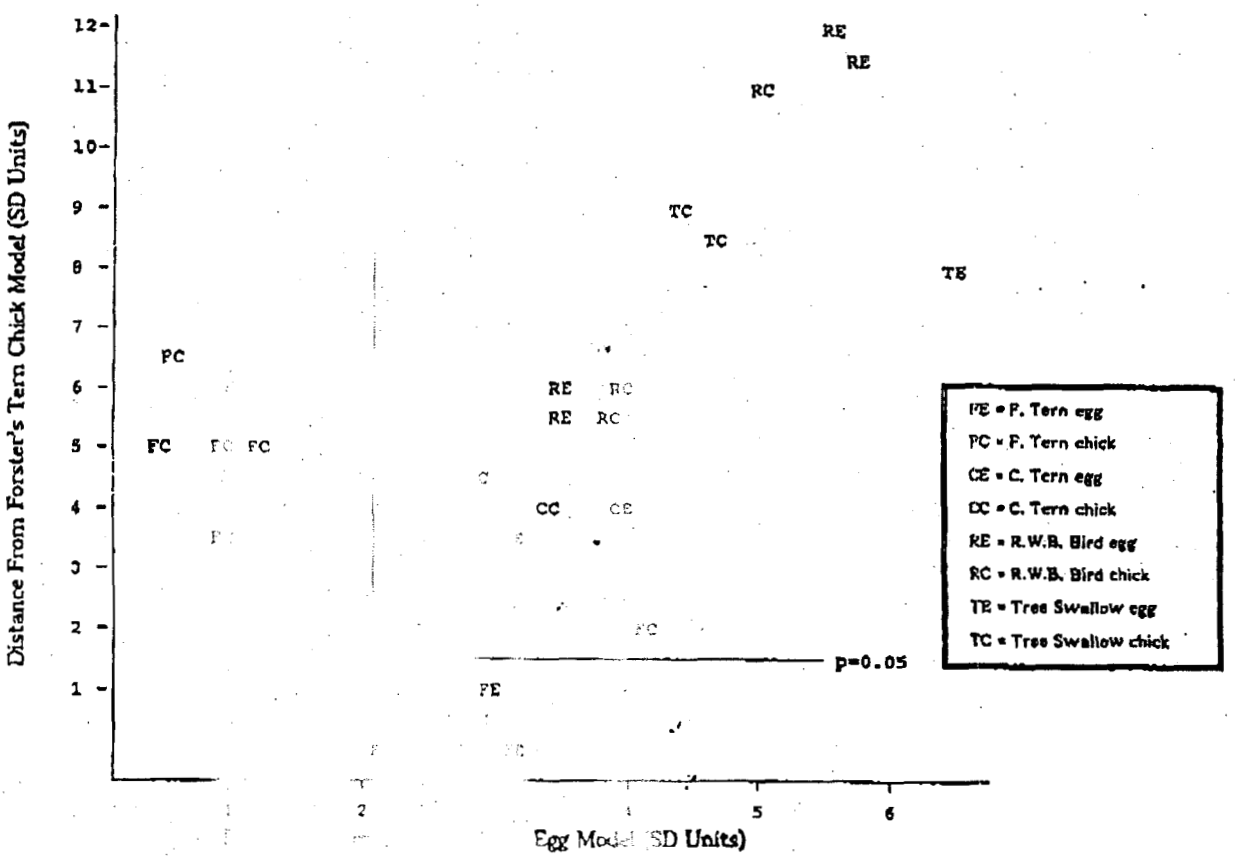

Fig. 7. Cooman's plot of [illegible] by the abscissa and the line parallel to abscissa-axis represents the 95% confidence level (*F*-test) for classific[illegible] tern egg-model. The area bound by the ordinate and the line parallel to the ordinate-axis is the 95% confidence level [illegible] tern chick-model

congeners by the yo[illegible] in the system. We also demo[illegible] of site-specific exposure of a[illegible] mulated via aquatic food chai[illegible] onjunction with appropriate [illegible], could prove to be useful f[illegible] al risk assessments. Ultimat[illegible] appropriate clean-up goals, for example [illegible] ontaminated systems like the lower [illegible] is *et al.* 1993). The tree swal[illegible] in this regard because of its [illegible] cts, and the ability to manipul[illegible] nt sediment contamination.

Although the relativ[illegible] rigorous statistical compari[illegible] in PCH concentrations, trend[illegible] h what would be expected bas[illegible] four test species, Forster's and [illegible] y piscivores, were similar [illegible] ions of PCHs than did the tree [illegible] ls, both of which are insectiv[illegible] on concentrations in tree s[illegible] than in red-winged blackbird[illegible] wo species were small. The [illegible] H concentrations in tree sw[illegible] uggest that further information is needed to determine what factors in the life histories of the species result in different exposure. It should be noted that of the four species studied, red-winged blackbirds were the only birds that may forage extensively in areas far from aquatic food chains (*i.e.*, in uplands).

Finally, the task of obtaining a comparable perspective of what relationships exist in environmental residue data by examining the concentration of individual constituents is formidable. However, in the present study it was demonstrated that it is possible to use PCA to compare profiles of PCB, PCDD and PCDF congeners in an environmental context and classify these PCHs into unique groups according to variables such as species, age, matrix, and geographical location.

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