2009

Persistence of organochlorine chemical residues in fish from the Tombigbee River (Alabama, USA): Continuing risk to wildlife from a former DDT manufacturing facility

Jo Ellen Hinck
U.S. Geological Survey (USGS), Columbia Environmental Research Center

Ross J. Norstrom
RJN Environmental, 1481 Forest Valley Drive, Ottawa, ON

Carl E. Orazio
U.S. Geological Survey (USGS), Columbia Environmental Research Center

Christopher J. Schmitt
U.S. Geological Survey (USGS), Columbia Environmental Research Center, cjschmitt@usgs.gov

Donald E. Tillitt
U.S. Geological Survey (USGS), Columbia Environmental Research Center

Environmental Pollution 157 (2009) 582–591

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Persistence of organochlorine chemical residues in fish from the Tombigbee River (Alabama, USA): Continuing risk to wildlife from a former DDT manufacturing facility

Jo Ellen Hinck [a,*], Ross J. Norstrom [b], Carl E. Orazio [a], Christopher J. Schmitt [a], Donald E. Tillitt [a]

[a] U.S. Geological Survey (USGS), Columbia Environmental Research Center (CERC), 4200 New Haven Road, Columbia, MO 65201, USA
[b] RJN Environmental, 1481 Forest Valley Drive, Ottawa, ON K1C 5P5, Canada

DDT persists in the environment near a former manufacturing facility that ceased production over 40 years ago, and concentrations represent a risk to fish and piscivorous birds in the area.

ARTICLE INFO

Article history:
Received 27 May 2008
Received in revised form 18 August 2008
Accepted 21 August 2008

Keywords:
Dichlorodiphenyl-trichloroethane
Pesticides
Superfund
Micropterus
Risk assessment

ABSTRACT

Organochlorine pesticide and total polychlorinated biphenyl (PCB) concentrations were measured in largemouth bass from the Tombigbee River near a former DDT manufacturing facility at McIntosh, Alabama. Evaluation of mean *p,p′*- and *o,p′*-DDT isomer concentrations and *o,p′*- versus *p,p′*-isomer proportions in McIntosh bass indicated that DDT is moving off site from the facility and into the Tombigbee River. Concentrations of *p,p′*-DDT isomers in McIntosh bass remained unchanged from 1974 to 2004 and were four times greater than contemporary concentrations from a national program. Total DDT in McIntosh bass exceeded dietary effect concentrations developed for bald eagle and osprey. Hexachlorobenzene, PCBs, and toxaphene concentrations in bass from McIntosh also exceeded thresholds to protect fish and piscivorous wildlife. Whereas concentrations of DDT and most other organochlorine chemicals in fish have generally declined in the U.S. since their ban, concentrations of DDT in fish from McIntosh remain elevated and represent a threat to wildlife.

Published by Elsevier Ltd.

1. Introduction

Dichlorodiphenyl-trichloroethane (DDT) was manufactured at a facility located along the Tombigbee River near McIntosh, Alabama from 1952 until 1963 (U.S Environmental Protection Agency (USEPA, 2006)). Pesticides, agricultural chelating agents, resins and additives used in the plastics industry, anti-oxidants, and small volume specialty chemicals were subsequently produced at the facility. The facility was listed as a National Priorities List (NPL) site in 1984 after lindane was detected in groundwater and DDT and its metabolites were detected in soil (USEPA, 2006). Under the Superfund Program, the USEPA organized the site into four operable units (OUs). One OU consisted of an effluent ditch and 370 acres of the Tombigbee River floodplain. This entire floodplain is typically inundated with water from December to April, creating a direct connection to the Tombigbee River. The effluent ditch and runoff from the waste disposal sites were the primary sources of contamination to the floodplain. The USEPA concluded that piscivorous wildlife feeding in the floodplain were at greatest risk from DDT and its primary metabolites, dichlorodiphenyl-dichloroethane (DDD) and dichlorodiphenyl-chloroethane (DDE). As part of the remedy, highly contaminated soils and sediments in the floodplain were excavated in 1998 to decrease DDT concentrations to an area-wide average of 15 $\mu g\ g^{-1}$. The remedial action to reduce DDT to acceptable concentrations would theoretically also reduce the concentrations of other contaminants of concern (ametryn, atrazine, butylbenzylphthalate, diazinon, prometon, prometryn, propazine, simazine, simetryn, terbuthylazine, terbutryn, tolban, chromium, copper, cyanide, mercury, and nickel) at the site (USEPA, 2006). Because contaminated soils and sediments were left on the floodplain, post-remediation monitoring was required. A monitoring goal to have whole-body DDT concentrations of 300–1500 ng g^{-1} in mosquitofish (*Gambusia affinis*) was not achieved in the five years of sampling after the remedial action. However, mean whole-body DDT concentrations in mosquitofish post-remediation (2000–22,000 ng g^{-1}) were generally lower than pre-remediation concentrations (14,000–41,000 ng g^{-1}). Based on these results, the USEPA concluded that leaving the DDT in the forested floodplain

* Corresponding author. Tel.: +1 573 876 1808; fax: +1 573 876 1896.
E-mail address: jhinck@usgs.gov (J.E. Hinck).

0269-7491/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.envpol.2008.08.021

continues to pose a risk to the piscivorous birds feeding in this area. In addition, fish likely move into the floodplain when the Tombigbee River floods, potentially increasing their exposure to DDT and its metabolites and providing a pathway for contaminants to move off site as the water recedes and returns to the main channel of the river. This timing is particularly important as it overlaps the beginning of the spawning season for some species including mosquitofish and largemouth bass (*Micropterus salmoides*). Previous studies have reported elevated concentrations of *p*,*p*′-DDE, total PCBs, hexachlorobenzene, and toxaphene in this portion of the Tombigbee River (USFWS, 1989, 1996; USEPA, 1995; Schmitt et al., 1999).

Fish and birds are sensitive to DDT exposure. Dietary exposure to technical DDT has reduced survival in fish at multiple life stages (see review by Jarvinen and Ankley, 1999), and protective thresholds for whole-body total DDT concentrations have been recommended for early life stage, juvenile, and adult fish (Beckvar et al., 2005). In addition, exposure to *p*,*p*′-DDE, *o*,*p*′-DDT, and *o*,*p*′-DDE can affect behavior and disrupt the endocrine and immune systems in fish (Donohoe and Curtis, 1996; Ungerer and Thomas, 1996; Faulk et al., 1999; Milston et al., 2003; Papoulias et al., 2003; Garcia-Reyero et al., 2006; Barber et al., 2007). Exposure to *p*,*p*′-DDE has been associated with reduced reproductive success of bird populations; bald eagle (*Haliaeetus leucocephalus*) and osprey (*Pandion haliaetus*) are especially susceptible to eggshell thinning after exposure (Anderson and Hickey, 1972; Wiemeyer et al., 1984, 1988). The potential effects of *o*,*p*′-DDT isomers to birds are largely unknown, and toxicity thresholds for avian receptors are not available for these metabolites.

Our first objective was to compare organochlorine pesticides and total PCB concentrations in largemouth bass from the Tombigbee River at McIntosh with other sites in the Mobile River basin. Concentrations of *p*,*p*′-DDT isomers in McIntosh bass were also compared to historical concentrations to determine if concentrations have declined and to contemporary concentrations from a national monitoring program. Our second objective was to examine ratios of *o*,*p*′- versus *p*,*p*′-isomers in total DDT to determine if the source of DDT in McIntosh bass could be identified. Lastly, a screening level risk evaluation was conducted to determine if contaminant concentrations pose a risk to fish and piscivorous birds.

2. Materials and methods

2.1. Study area and sampling sites

The Mobile River basin comprises two large rivers, the Tombigbee and the Alabama, which meet to form the Mobile River in southwestern Alabama; the Mobile River ultimately flows into Mobile Bay and the Gulf of Mexico (Fig. 1). The main site of interest was located on the lower Tombigbee River near a former DDT manufacturing facility and a former chlor-alkali facility in the city of McIntosh. Both facilities are NPL sites, and the main contaminants of concern are DDT, mercury, and chlorinated benzenes. Sites located on the Coosa River at Childersburg, the Alabama River at Eureka Landing, the Tombigbee River at Lavaca, and the Mobile River at Bucks were being sampled as part of a national monitoring program study and expected to have relatively low concentrations of DDT (Hinck et al., 2008) and were therefore included for comparison with the McIntosh site.

2.2. Fish sampling

Largemouth bass were captured by electrofishing in October 2004 (Fig. 1). Ten (each) adult male and female fish were collected per site where possible (Table 1). Fish were euthanized, weighed, and measured. All collection, handling, and euthanasia procedures followed animal care and use guidelines (American Fisheries Society et al., 2004). Whole-fish were wrapped in aluminum foil and shipped to the analytical laboratory on ice. Samples were stored at −20 °C until analyzed.

2.3. Laboratory analyses

Fish from Childersburg, Lavaca, Eureka Landing, and Bucks were analyzed as whole-body composite samples (Hinck et al., 2008); stomach contents were included in the samples. Individual fish were partly thawed, cut into pieces, and ground to a fine texture. Fifteen percent of the total body weight was sub-sampled (45–83 g) to maintain the proportional size and contaminant load representation of each fish. The ground sub-samples were then grouped to create a single homogeneous composite sample representing each gender–site combination; i.e. one female and one male composite sample per site (total $n = 8$). The composite sample was then sub-sampled (200 g) and re-frozen (−20 °C). Contaminant concentrations were analyzed in individual fish from McIntosh ($n = 4$ females; $n = 6$ males) because of high DDT concentrations measured historically in fish from this site. Individual fish were homogenized as described previously and sub-sampled for contaminant analysis. All equipment was disassembled and chemically cleaned between samples to prevent cross-contamination.

The fish samples were analyzed for *o*,*p*′-DDE, *o*,*p*′-DDD, *o*,*p*′-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD, *p*,*p*′-DDT, pentachlorobenzene, hexachlorobenzene, and total PCBs using procedures described previously (Hinck et al., 2008). In summary, a 10 g subsample of each homogenized sample was dehydrated with anhydrous sodium sulfate, spiked with recovery standards (PCB 029, PCB 155, PCB 204, and *p*,*p*′-DDD-*d*8), column extracted with dichloromethane, and subsequently cleaned up using size exclusion and adsorption column cleanup procedures. The extracts were then applied to a two-layered octadecyl silica/activated silica gel column and separated into two fractions, one fraction containing PCBs with selected pesticides and a second fraction containing the remainder of the pesticides. The sample extracts were adjusted to a final volume of 1 mL. Two instrumental internal standards, PCB 030 and 207, were used. The analytes were quantified by dual column high-resolution gas chromatographic (GC) system with electron capture detection (ECD). Analyses were performed using Hewlett–Packard 5890 Series II GCs (Agilent, Palo Alto, CA) with cool on-column capillary injection systems and Hewlett–Packard model 7673 autosamplers. Each analytical column, 60-m × 0.25-mm × 0.25 μm DB-5 (5% phenyl, 95% methylsilicone) and DB-17 (50% phenyl, 50% methylsilicone; Agilent, Palo Alto, CA), had a deactivated capillary retention gap attached. The hydrogen carrier gas was pressure regulated at 25 psi. The chromatographic temperature program was initial temperature 60 °C, immediately ramped to 150 °C at 15 °C/min, then ramped to 250 °C at 1 °C/min, and finally ramped to 320 °C at 10 °C/min and held for 1 min. The GC/ECD data were collected, archived in digital form, and processed using a PerkinElmer chromatography data system. Total PCBs were reported as the sum of 139 congeners. Toxaphene residues were quantified on the basis of 20 component peaks of a technical toxaphene standard. Mean percent recovery for the recovery standards ranged from 85 ± 4 to 105 ± 8%. Matrix spike recoveries ranged from 91 to 108%. The limit-of-detection (LOD) for each compound was calculated by adding the average procedural blank concentration to three times the procedural blank standard deviation (Keith, 1991). The LODs were 0.81 ng g^{-1} wet weight (ww) for *o*,*p*′-DDE; 0.10 ng g^{-1} ww for *o*,*p*′-DDD; 0.10 ng g^{-1} ww for *o*,*p*′-DDT; 2.4 ng g^{-1} ww for *p*,*p*′-DDE; 0.18 ng g^{-1} ww for *p*,*p*′-DDD; 0.47 ng g^{-1} ww for *p*,*p*′-DDT; 0.07 ng g^{-1} ww for pentachlorobenzene; 0.14 ng g^{-1} ww for hexachlorobenzene; 61 ng g^{-1} ww for total PCBs; and 10 ng g^{-1} ww for toxaphene.

2.4. Statistical analysis

Contaminant concentrations were analyzed statistically as wet weight values and were $\log_{10}$-transformed. Mean contaminant concentrations and lipid content for female and male bass from McIntosh were calculated and used to compare to concentrations in the composite samples. Means for both types of samples (individual fish and whole-body composites) are based on the proportional size representation of each fish in the sample (i.e. weighted arithmetic mean) and are therefore directly comparable. A total of 10 samples (one male and one female from each site) were included in the statistical analysis. Gender and site differences in contaminant concentrations and lipid content were evaluated with one-way analysis of variance (ANOVA) followed by Tukey's posthoc test. The α-level was 0.05. Gender differences in contaminant concentrations were not significant; therefore, male and female samples were combined to represent the mean site concentration. A value of one-half the LOD was substituted for censored values in all statistical analysis. All computations and statistical analyses were performed with Version 9.1 of SAS (Cary, NC).

2.5. Temporal and spatial trend analysis

Temporal and spatial trends in contaminant concentrations were examined using historical and contemporary data. The McIntosh and Eureka Landing sites were National Contaminant Biomonitoring Program (NCBP) sites (Sites 14 and 59, respectively) where fish were sampled from 1969 to 1986 (Schmitt et al., 1999). Concentrations of *p*,*p*′-DDE, *p*,*p*′-DDD, and *p*,*p*′-DDT in bass from McIntosh and Eureka Landing were compared to historical NCBP concentrations. Concentrations in bass from McIntosh were compared to *p*,*p*′- and *o*,*p*′-isomers, pentachlorobenzene, hexachlorobenzene, toxaphene, and total PCBs' concentrations in largemouth bass from the U.S. Geological Survey's BEST Program (Schmitt, 2002; Schmitt et al., 2005; Hinck et al., 2006, 2007, 2008). Briefly, chemical contaminants were measured in piscivorous and benthivorous fish collected from 1995 to 2004. Collection sites represented a range of contaminant sources (e.g. mining, agriculture, industry, and urban areas) and key points on major rivers such as dams and tributary confluences. Some BEST Program sites were located near former DDT manufacturing facilities and agricultural areas with high historical use of technical DDT.

Fig. 1. Bass collection sites in the Mobile River basin.

2.6. Isomeric comparisons

Technical-grade DDT contains an average of 18% *o,p′*-DDT (Buser and Müller, 1995). The main sources of DDT in the environment are historical application of technical DDT, atmospheric deposition, dicofol manufacturing and application, and wastes from DDT manufacturing facilities. The percentage of *o,p′*- versus *p,p′*-isomers in total DDT was examined to determine if proportions were similar among sites and to identify the potential source of DDT in the fish samples.

Table 1
Collection date, sample size (*n*), and mean (±standard error) length and weight of largemouth bass from the Mobile River basin

Site	Collection date in 2004	Female			Male		
		n	Length (mm)	Weight (g)	*n*	Length (mm)	Weight (g)
Childersburg	10/14–10/15	10	457 ± 16	1405 ± 143	10	407 ± 13	974 ± 110
Eureka Landing	10/6–10/7	10	410 ± 18	948 ± 120	10	392 ± 18	790 ± 141
Lavaca	10/12–10/13	11	391 ± 21	798 ± 160	8	356 ± 18	591 ± 115
McIntosh	10/11	4	434 ± 20	1144 ± 196	6	420 ± 23	1015 ± 171
Bucks	10/8–10/9	12	426 ± 12	1041 ± 118	8	401 ± 11	807 ± 62

2.7. Screening level risk evaluation

Contaminant concentrations were compared to toxicity thresholds and wildlife toxicity values from the scientific literature to screen for risk. Criteria for inclusion of a toxicity threshold were that the threshold was based on a whole-body fish concentration and was associated with reproductive performance, growth, or survival in fish. Wildlife toxicity values focused on avian receptors because birds are known to be particularly sensitive to DDT isomers, hexachlorobenzene, and PCBs. A PCB toxicity value for American mink (*Mustela vison*) was also included because this species is sensitive to PCB exposure (Aulerich and Ringer, 1977).

A more extensive risk screening was conducted for *p,p′*-DDE because of the historical DDT contamination at the McIntosh site. The risk of *p,p′*-DDE to piscivorous birds was evaluated with models based on dietary exposure for bald eagle and osprey. Both of these species consume large, adult fish such as largemouth bass. Bald eagle, osprey, and other piscivorous and omnivorous birds forage and nest in the Mobile–Tensaw Delta and elsewhere in southern Alabama. Models assuming a diet of 100% fish were used to screen for risk; site-specific data for

other exposure pathways such as water and sediment were not available for all sites and were not considered in this risk evaluation. Tissue-based toxicity reference values (TRVs) developed from egg concentrations were used because developing embryos are more sensitive to *p,p′*-DDE than adult birds (Wiemeyer et al., 1988; Elliott and Harris, 2001). A dietary effect concentration (DEC) was calculated for each species modeled using the equation DEC ($\mu g\ g^{-1}$) = [tissue-based TRV (mg/kg egg)/biomagnification factor $(BMF)_{fish \rightarrow egg}$]. The TRV for bald eagle (6 mg kg^{-1} egg) was based on a threshold suggested by Elliott and Harris (2001). The TRV for osprey (4.2–8.7 mg kg^{-1} egg) was based on a range of concentrations that resulted in severe eggshell thinning (15–20%; Wiemeyer et al., 1988) and associated reproductive problems in osprey populations (Anderson and Hickey, 1972). The BMFs of *p,p′*-DDE in osprey and bald eagle eggs were 47 for both species based on equations developed by Norstrom et al. (2007), and the resulting DECs were 130 ng g^{-1} for bald eagle and 90–190 ng g^{-1} for osprey. Piscivorous birds may be at risk from *p,p′*-DDE if the measured concentration in the fish sample exceeded the DEC.

3. Results and discussion

3.1. Lipid content and contaminant concentrations

3.1.1. Lipid content

Mean lipid content ranged from 2.3 to 5.5% and was significantly lower in bass from Lavaca than those from Childersburg, Eureka Landing, and McIntosh (Table 2).

3.1.2. *p,p′*- and *o,p′*-DDT isomers

Mean concentrations of *p,p′*-isomers were generally greater than *o,p′*-isomers in bass from the Mobile River basin. Mean concentrations of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT were significantly greater in bass from McIntosh than those from other sites (Table 2). The mean *p,p′*-DDE concentration was 4714 ng g^{-1} in McIntosh bass but was only 19–81 ng g^{-1} at all other sites. Concentrations of *p,p′*-DDD were low (3.5–8.9 ng g^{-1}) in bass from Childersburg, Eureka Landing, Lavaca, and Bucks compared to the mean concentration at McIntosh (1856 ng g^{-1}). Mean *p,p′*-DDT concentrations were also elevated in bass from McIntosh (376 ng g^{-1}) compared to the other sites (1.4–2.8 ng g^{-1}). Similar site trends were evident for *o,p′*-isomers with concentrations being at least 100-fold greater in McIntosh bass (Table 2). Mean *o,p′*-DDE concentrations were significantly greater in McIntosh bass (1246 ng g^{-1}) than those from other sites (0.9–9.3 ng g^{-1}). The mean *o,p′*-DDD concentration was 780 ng g^{-1} in McIntosh bass but was significantly lower (0.2–1.9 ng g^{-1}) in bass from other sites. The mean *o,p′*-DDT concentration in McIntosh bass was 73 ng g^{-1}; *o,p′*-DDT was not detected (<0.1 ng g^{-1}) in bass from Childersburg, Eureka Landing, Lavaca, or Bucks.

Total DDT (sum of *o,p′*- and *p,p′*-DDE, DDD, and DDT) concentrations in individual bass from McIntosh ranged from 419 to 49,810 ng g^{-1} and were greater than concentrations in bass from Childersburg (59–72 ng g^{-1}), Eureka Landing (35–39 ng g^{-1}), Lavaca (24–27 ng g^{-1}), and Bucks (94–113 ng g^{-1}). The primary DDT metabolite *p,p′*-DDE (110–27,100 ng g^{-1}) was the greatest contributor of total DDT in all McIntosh samples (39–74%). Concentrations of *p,p′*-DDT (5–2050 ng g^{-1}), *p,p′*-DDD (20–9500 ng g^{-1}), *o,p′*-DDE (10–6600 ng g^{-1}), *o,p′*-DDD (9–4200 ng g^{-1}), and *o,p′*-DDT (1–360 ng g^{-1}) collectively contributed 26–61% to the total DDT concentrations in bass from McIntosh.

Relatively high DDT concentrations were reported historically in bass near McIntosh and were attributed to the former DDT manufacturing facility (Schmitt et al., 1999; USFWS, 1989, 1992, 1996). Concentrations of *p,p′*-DDE in whole-body bass from McIntosh were 1210–15,000 ng g^{-1} from 1969 to 1984 (Schmitt et al., 1999) and 780–4130 ng g^{-1} in 1992 (USFWS, 1996); concentrations of *p,p′*-DDD (160–4560 ng g^{-1}) and *p,p′*-DDT (40–1030 ng g^{-1}) were also high in these samples. Concentrations of *o,p′*-DDE (170–5160 ng g^{-1}), *o,p′*-DDD (20–3550 ng g^{-1}), and *o,p′*-DDT (70–2730 ng g^{-1}) in bass from McIntosh in 1992 were considered high (USFWS, 1996). Elevated total DDT concentrations in bass from this area (8000 ng g^{-1}) were also reported in a 1990 study (USFWS, 1992) and later in a 1992 study of this same area (1240−21,160 ng g^{-1}; USFWS, 1996).

3.1.3. Chlorinated benzenes

Mean concentrations of pentachlorobenzene and hexachlorobenzene were significantly greater in bass from McIntosh than from Childersburg, Eureka Landing, and Lavaca (Table 2). Pentachlorobenzene was not detected (0.07 ng g^{-1}) in bass from Childersburg, Eureka Landing, and Lavaca, whereas mean pentachlorobenzene concentrations were 10.7 ng g^{-1} at McIntosh and 0.2 ng g^{-1} at Bucks (Table 2). Mean concentrations of hexachlorobenzene were low (0.2–1.5 ng g^{-1}) in bass from Childersburg, Eureka Landing, Lavaca, and Bucks compared to McIntosh (213 ng g^{-1}). Elevated concentrations of chlorinated benzenes have been documented in soil and sediment from the floodplain on the NPL sites at McIntosh (USEPA, 1995). Among other sources, chlorinated benzenes such as hexachlorobenzene are formed in the electrolytic cells of chlor-alkali plants as a result of chlorine reacting with graphite anode materials. Hexachlorobenzene concentrations in McIntosh bass were lower in the present study (213 ng g^{-1}) than in 1984 (410 ng g^{-1}; Schmitt et al., 1999).

3.1.4. Toxaphene

Mean concentrations of toxaphene were significantly greater in bass from McIntosh (104 ng g^{-1}) than from Childersburg, Eureka Landing, and Bucks (12–30 ng g^{-1}; Table 2). Toxaphene was the most heavily used insecticide in the United States following the 1972 DDT ban. Use of toxaphene in the United States peaked in the late 1970s, and the pesticide was subsequently also banned. Historical NCBP concentrations of toxaphene were <50–300 ng g^{-1} in McIntosh bass from 1971 to 1984 (Schmitt et al., 1999), which is similar to the mean concentration (104 ng g^{-1}) from this study.

Table 2
Mean (±standard error) concentrations (ng g^{-1}) of contaminants in largemouth bass

Analyte	Childersburg	Eureka Landing	Lavaca	McIntosh	Bucks	$F_{4,5}$	p
Lipid (%)	4.5 ± 0.5b	4.6 ± 0.0b	2.3 ± 0.3a	5.5 ± 0.3b	3.7 ± 0.5ab	11.80	0.01
p,p′-DDE	60 ± 9.5a	29 ± 1.5a	19 ± 1.5a	4714 ± 3613b	81 ± 4.5a	19.29	<0.01
p,p′-DDD	4.1 ± 2.4a	3.5 ± 0.2a	3.7 ± 0.4a	1856 ± 1492b	8.9 ± 1.4a	18.33	<0.01
p,p′-DDT	1.4 ± 0.5a	1.7 ± 0.0a	2.2 ± 0.3a	376 ± 291b	2.9 ± 0.6a	18.74	<0.01
o,p′-DDE	0.9 ± 0.0a	3.1 ± 0.1a	1.0 ± 0.1a	1246 ± 997b	9.3 ± 2.4a	29.85	<0.01
o,p′-DDD	0.2 ± 0.1a	0.4 ± 0.0a	0.2 ± 0.0a	780 ± 660b	1.9 ± 0.5a	21.74	<0.01
o,p′-DDT	0.1 ± 0.0a	0.1 ± 0.0a	0.1 ± 0.0a	73 ± 556b	0.1 ± 0.0a	46.28	<0.01
Pentachlorobenzene	0.1 ± 0.0a	0.1 ± 0.0a	0.1 ± 0.0a	10.7 ± 9.3b	0.2 ± 0.2ab	8.05	0.02
Hexachlorobenzene	0.4 ± 0.1a	0.5 ± 0.0a	0.2 ± 0.0a	213 ± 159b	1.5 ± 0.2a	32.06	<0.01
Toxaphene	13 ± 8a	20 ± 0a	30 ± 10a	104 ± 25b	25 ± 5a	8.79	0.02
Total PCBs	2100 ± 600b	230 ± 0a	185 ± 25a	714 ± 311ab	215 ± 35a	14.83	<0.01

For each contaminant, means with the same letter do not differ significantly from each other ($p < 0.05$); $n = 2$ for all sites except McIntosh ($n = 10$).

3.1.5. Total PCBs

Mean total PCB concentrations were greater in bass from McIntosh (714 ng g^{-1}) than from Eureka Landing, Lavaca, and Bucks (185–230 ng g^{-1}), but these differences were not statistically significant (Table 2). The mean PCB concentration was greatest at Childersburg (2100 ng g^{-1}; Table 2). Total PCB concentrations in bass near McIntosh were lower (140–350 ng g^{-1}) in 1992 compared to the present study (USFWS, 1996); however, it is unclear which PCB congeners were included in the USFWS study. Although not directly comparable to total PCB concentrations in the present study, Aroclor 1254 concentrations were <100–1300 ng g^{-1} in McIntosh bass from 1969 to 1984 (Schmitt et al., 1999).

3.2. Temporal and spatial trends of p,p′- and o,p′-DDT isomer concentrations

Temporal trends in *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT concentrations in bass from historical NCBP sampling sites, McIntosh and Eureka Landing, were examined; *o,p′*-isomers were not reported by the NCBP. The routine measurement of DDT isomers in the early 1970s was plagued by chromatographic interference from PCBs, toxaphene, and other organochlorine residues. Under the quality assurance and methods development component of the National Pesticide Monitoring Program (the forerunner of the NCBP), largemouth bass samples from McIntosh were re-analyzed by methods considered to be the best available at the time. The analyses included the separation of PCBs from other organochlorine residues by silica gel/silicic acid chromatography and the quantification of toxaphene residues; procedures that were subsequently incorporated into routine NCBP analyses (Schmitt, 1981). Concentrations of PCBs in bass from McIntosh increased in 1971 but were low in 1972, a period when DDT concentrations rose sharply. Toxaphene concentrations were also low relative to those of the *p,p′*-DDT isomers at this time. Collectively, these results and those of the routine analyses (Fig. 2) indicate that DDT concentrations rose sharply at McIntosh in 1972, and the rise was not likely to be attributable to interferences by PCBs and toxaphene. Low *p,p′*-DDD and *p,p′*-DDT concentrations in 1973 bass from Eureka Landing were potentially related to a laboratory reporting issue as concentrations in later years were greater and followed a more steady decline. Similar temporal trends were evident for bass from the Hudson River at Poughkeepsie, New York; the Potomac River at Little Falls, Maryland; the Truckee River at Fernley, Nevada; and the Klamath River at Hornbrook, California, with dips in concentrations of *p,p′*-DDD and *p,p′*-DDT during 1973 (Schmitt et al., 1999).

Overall, concentrations of *p,p′*-isomers were greater in McIntosh bass than in Eureka Landing bass (Fig. 2). Concentrations of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT generally declined in bass from Eureka Landing between 1974 and 2004, whereas concentrations at McIntosh were persistent. Historical *p,p′*-DDE concentrations were 3260–15,000 ng g^{-1} in McIntosh bass and 210–1270 ng g^{-1} in Eureka Landing bass (Fig. 2). Concentrations of *p,p′*-DDE decreased from 230 to 29 ng g^{-1} in bass from Eureka Landing between 1986 and 2004, but concentrations were similar at McIntosh in 1984 (4710 ng g^{-1}) and 2004 (4714 ng g^{-1}). Historical *p,p′*-DDD concentrations were greater at McIntosh (280–1800 ng g^{-1}) than at Eureka Landing (5–590 ng g^{-1}; Fig. 2). From 1986 to 2004, *p,p′*-DDD concentrations decreased from 40 to 4 ng g^{-1} at Eureka Landing, but concentrations at McIntosh increased from 1160 to 1856 ng g^{-1} from 1984 to 2004 (Fig. 2). Historical *p,p′*-DDT concentrations were 280–1800 ng g^{-1} at McIntosh and 5–660 ng g^{-1} at Eureka Landing (Fig. 2). Concentrations of *p,p′*-DDT decreased from 20 to 2 ng g^{-1} at Eureka Landing from 1986 to 2004 but increased from 280 to 376 ng g^{-1} at McIntosh between 1984 and 2004 (Fig. 2). These data indicate that DDT continues to move off site from the manufacturing facility and persists in fish near the facility.

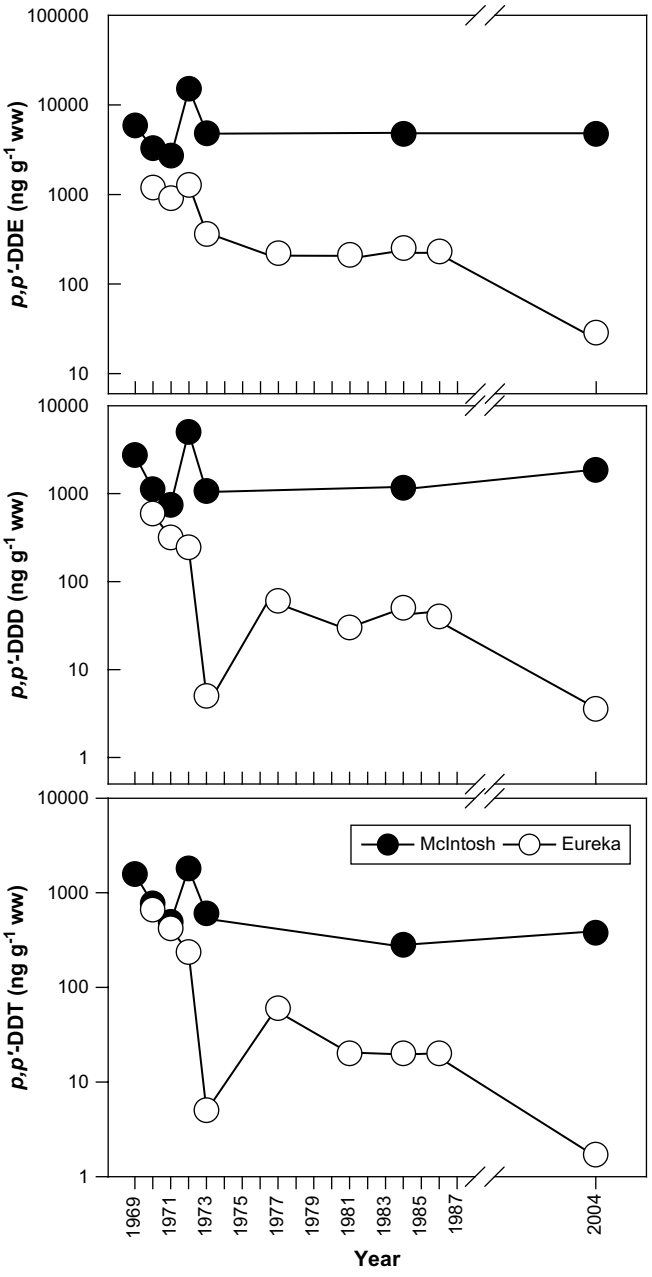

Fig. 2. Trends in *p,p′*-DDT isomer concentrations in largemouth bass from National Contaminant Biomonitoring Program sites.

Concentrations of *o,p′*- and *p,p′*-DDE, DDD, and DDT in bass from the BEST Program were compared to concentrations at McIntosh (Schmitt, 2002; Schmitt et al., 2005; Hinck et al., 2006, 2007, 2008); these data included largemouth bass from the Mississippi, Rio Grande, Columbia, Colorado, Pee Dee, Savannah, and Apalachicola River basins. Concentrations in whole-body composites samples ($n = 99$) representing bass from 51 sites were 0.21–17 ng g^{-1} for *o,p′*-DDE; 0.05–320 ng g^{-1} for *o,p′*-DDD; 0.05–240 ng g^{-1} for *o,p′*-DDT; 5–2700 ng g^{-1} for *p,p′*-DDE; 0.34–280 ng g^{-1} for *p,p′*-DDD; and 0.24–310 ng g^{-1} for *p,p′*-DDT between 1995 and 2004. The mean total DDT concentration in bass from all BEST Program sites was 197 ng g^{-1} (Fig. 3). Mean total DDT concentrations were at least four times greater in bass from McIntosh (9045 ng g^{-1}) than any BEST Program site (10–2233 ng g^{-1}; Fig. 3). High total DDT concentrations in bass from Site 325 (Gila River at Arlington, Arizona) were attributed to high technical DDT applications rates in

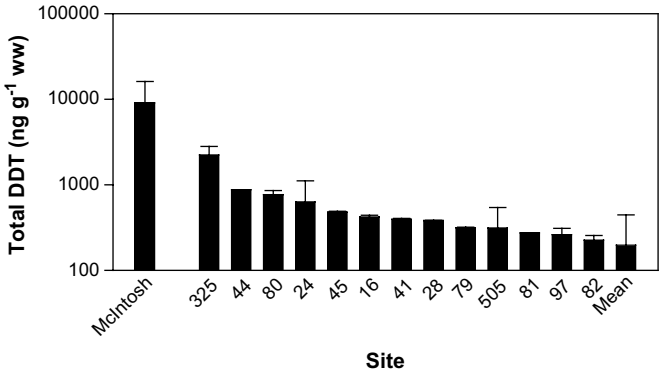

Fig. 3. Mean (±standard error) concentrations of total DDT (*o,p′*- and *p,p′*-DDE, DDD, and DDT) in largemouth bass from McIntosh and BEST Program sites. The mean of all BEST Program sites (n = 51) is also presented, and only BEST Program sites with concentrations greater than the overall mean are graphed. 325, Gila R. at Arlington, AZ; 44, Yakima R. at Granger, WA; 80, Yazoo R. at Redwood, MS; 24, Ohio R. at Marietta, OH; 45, Willamette R. at Oregon City, OR; 16, Rio Grande at Mission, TX; 41, Snake R. at Hagerman, ID; 28, Arkansas R. at Pine Bluff, AR; 79, Canadian R. at Eufaula, OK; 505, Willamette R. at Portland, OR; 81, Red R. at Alexandria, LA; 97, Columbia R. at Pasco, WA; 82, Red R. at Lake Texoma, TX/OK.

agricultural areas (Hinck et al., 2007); high total DDT concentrations (225–875 ng g^{-1}) at other BEST Program sites (Sites 41, 44, 45, 97, and 505 in the Columbia River basin; Site 16 in the Rio Grande basin; and Sites 79–82 in the Mississippi River basin) were also related to agricultural applications rather than DDT production facilities (Schmitt, 2002; Schmitt et al., 2005; Hinck et al., 2006). In contrast, DDT was manufactured near Site 24 (Ohio River at Marietta, Ohio) and Site 28 (Arkansas River at Pine Bluff, Arkansas; Schmitt, 2002), but the mean concentrations at these sites (383–631 ng g^{-1}) were more than 10-fold lower than at McIntosh (Fig. 3). Overall, total DDT concentrations in bass from McIntosh were greater than any concentration measured by the national monitoring program.

3.3. Isomeric comparisons

The most common type of concentration data for DDT is that of soils and sediments. Investigations conducted as part of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) activities at the two adjacent NPL sites at McIntosh (Ciba–Geigy Corporation, 1994; Woodward-Clyde, 1994) found that the mean percentage of *o,p′*-isomers in total DDT (47%) of floodplain sediments was greater than that expected from technical formulations of DDT (18%); mean percentages of *o,p′*- versus *p,p′*-isomers were 61% *o,p′*-DDE, 43% *o,p′*-DDD, and 54% *o,p′*-DDT. Venkatesan et al. (1996) also reported high mean *o,p′*-DDE to *p,p′*-DDE percentages in sediments (31%) and tar cake (40%) from a site contaminated by DDT manufacturing acid wastes.

The high concentrations and unique patterns of *o,p′*- and *p,p′*-isomer concentrations in bass from McIntosh indicate a local source of DDT in this part of the Tombigbee River. Provided dicofol sources of DDT can be ruled out, *o,p′*-isomers exceeding 18% of total DDT in sediments indicate that the DDT source is DDT manufacturing acid wastes rather than the use of DDT as a pesticide (Venkatesan et al., 1996). Similar data for determining the source or sources of *o,p′*-isomers in fish are not available. Few studies have documented the metabolism of *o,p′*-isomers in fish; therefore, it is unknown whether the degradation rates of *o,p′*-isomers are equal in fish and sediments. However, the *o,p′*- and *p,p′*-isomer ratios in bass from McIntosh parallel the sediment isomer ratios from the site, which indicates that the fish have some site fidelity in order to maintain this signal even though they feed over a larger area. Looser et al. (2000) reported that the percentages of *o,p′*-DDT and *p,p′*-DDT in open sea fish were comparable to technical DDT and concluded that DDT accumulation and metabolism were unselective. In addition, *p,p′*-isomer concentrations were generally greater than *o,p′*-isomers in bass from BEST Program sites, where *o,p′*-isomers comprised <14% of total DDT concentrations (Hinck et al., 2007, 2008). These studies also found that fish with the greatest *o,p′*-isomer concentrations were from areas with high historical technical DDT application rates (Hinck et al., 2007, 2008).

The percentage of *o,p′*-isomers to *p,p′*-isomers differed among sites in the Mobile River basin (Fig. 4). Small percentages of *o,p′*-DDE (1–5%), *o,p′*-DDD (4–5%), and *o,p′*-DDT (2–3%) were present in bass from Childersburg and Lavaca. The percentages of *o,p′*-DDE (10%) and *o,p′*-DDD (11–17%) were greater than *o,p′*-DDT (2–3%) in bass from Eureka Landing and Bucks. The percentages of *o,p′*- versus *p,p′*-isomers were greater in McIntosh bass, which contained 21% *o,p′*-DDE, 30% *o,p′*-DDD, and 16% *o,p′*-DDT, compared to other sites (Fig. 4). Mean percentages of *o,p′*-DDE (44%), *o,p′*-DDD (36%), and *o,p′*-DDT (60%) were high in bass from McIntosh in 1990 (USFWS, 1992). CERCLA investigations at the two NPL sites at McIntosh also reported elevated mean percentages of *o,p′*-DDE (23%), *o,p′*-DDD (24%), and *o,p′*-DDT (39%) in bass (Ciba–Geigy Corporation, 1994; Woodward-Clyde, 1994). Mean total *o,p′*-isomers in total DDT were greater in bass from McIntosh (23%) and Bucks (11%) compared to those from other sites (2–10%). The source of relatively high *o,p′*-isomer concentrations in fish from Bucks is probably sediment being transported downstream from McIntosh (e.g. sediment re-suspension during flood events). Such high percentages of *o,p′*-isomers have not been documented in fish from other sites; the results indicate that the local source of DDT is likely the former manufacturing facility.

3.4. Screening level risk evaluation

3.4.1. *p,p′*- and *o,p′*-DDT isomers

Concentrations of *p,p′*-DDE in McIntosh bass exceeded protective thresholds for fish and DECs for piscivorous birds. Total DDT concentrations exceeding 600 ng g^{-1} may be harmful to juvenile and adult fish (Beckvar et al., 2005). Applying this threshold, total and *p,p′*-DDE concentrations were >600 ng g^{-1} in eight of ten bass from McIntosh (Fig. 5). Concentrations of total DDT (24–113 ng g^{-1}) and *p,p′*-DDE (17–85 ng g^{-1}) in bass from Childersburg, Eureka Landing, Lavaca, and Bucks did not exceed this threshold (Fig. 5).

Field-estimated BMFs are available for bald eagle and osprey (e.g. Giesy et al., 1995; Henny et al., 2003), but we derived the DECs for *p,p′*-DDE using calculated BMFs to more accurately predict concentrations that pose a risk to bald eagle and osprey.

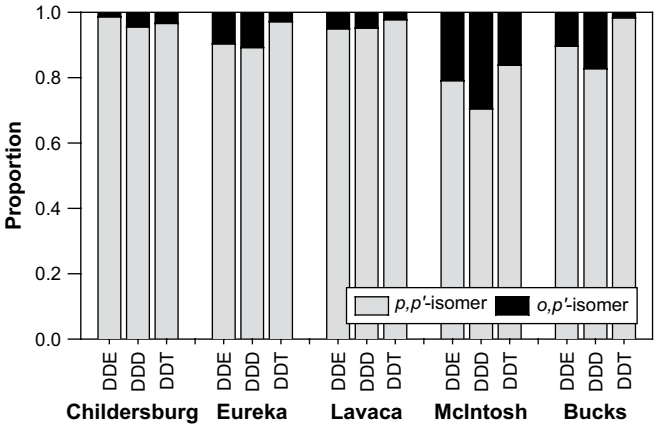

Fig. 4. Mean proportions of *o,p′*- and *p,p′*-DDT isomers in largemouth bass.

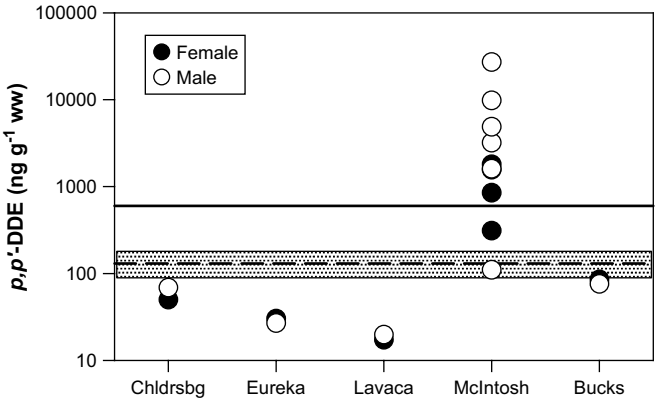

Fig. 5. Concentrations of *p,p′*-DDE in largemouth bass. Reference lines on the graph include a toxicity threshold to protect juvenile and adult fish (600 ng g^{-1}; Beckvar et al., 2005) and dietary effect concentrations for bald eagle (130 ng g^{-1}) and osprey (90–190 ng g^{-1}; see text for calculation).

Specifically, a bioaccumulation model for lipophilic contaminants that predicts the BMF of *p,p′*-DDE in herring gull (*Larus argentatus*) eggs was used to estimate BMFs in bald eagle and osprey eggs (Norstrom et al., 2007). The calculation used annual average daily food intake, which was estimated using the allometric relationship between field metabolic rate and body weight (W_B; Williams et al., 1993). The clearance rate constants of *p,p′*-DDE were calculated from the value in herring gulls (Norstrom et al., 2007) and adjusted as a function of $(W_B)^{-0.3}$ (Glaser and Connolly, 2002). The calculations were based on a 5 kg female eagle and a 1.5 kg female osprey with an average of 10% whole-body fat content laying two eggs. Partitioning between plasma and fat, efficiency of contaminant uptake, and egg/whole-body concentration ratio were assumed the same as for herring gulls (Norstrom et al., 2007). The calculated BMFs of *p,p′*-DDE in osprey eggs (47) and eagle eggs (47) were similar to the calculated BMF for the herring gull (55; Norstrom et al., 2007). These calculated BMFs were between field-estimated BMFs of 22 for bald eagle (Giesy et al., 1995) and 87 for osprey (Henny et al., 2003). Field-estimated BMFs of slowly excreted contaminants such as *p,p′*-DDE are subjected to considerable error because it is impossible to accurately estimate the true exposure of the bird that results in the egg residues. The true BMFs for bald eagle and osprey are unlikely to be greater than that in the herring gull given their relative body weights. The exposure of the osprey was probably underestimated because the field BMF was based only on food eaten during the nesting season (Henny et al., 2003). The bald eagle field BMF, which was based on food items collected September–December and March–May (Giesy et al., 1995), is more likely to be accurate but does not account for diet during winter migration or individual variation in exposure due to species and size of fish eaten. Nine of ten bass from McIntosh had *p,p′*-DDE concentrations that exceeded the DEC for bald eagle (130 ng g^{-1}); bass from other Mobile River basin sites did not exceed the bald eagle DEC (Fig. 5). Concentrations of *p,p′*-DDE in bass from McIntosh but not Childersburg, Eureka Landing, Lavaca, or Bucks also exceeded the DEC for osprey (90–190 ng g^{-1}; Fig. 5). Overall, these data indicate that *p,p′*-DDE risk to fish, osprey, and bald eagle was greatest at McIntosh.

The USEPA (2006) concluded that the remediation efforts in the floodplain adjacent to the Tombigbee River failed to reduce DDT concentrations in mosquitofish to ecologically acceptable levels (300–1500 ng g^{-1}), and therefore it continues to pose a risk to the piscivorous birds feeding in the open areas of the floodplain. These contaminated fish represent a biological pathway for DDT to leave the floodplain and enter the Tombigbee River, where they may be consumed by piscivorous fish and wildlife. The elevated *o,p′*- and *p,p′*-isomer concentrations in bass from our study further indicates that DDT is being transported into the Tombigbee River.

Although the *o,p′*-isomers historically were considered relatively benign, recent studies have determined that *o,p′*-isomers are endocrine active. Dietary exposure to *o,p′*-DDT and *o,p′*-DDE can affect liver and gonad size, plasma vitellogenin concentrations, and lipid levels in fish (Donohoe and Curtis, 1996; Ungerer and Thomas, 1996; Papoulias et al., 2003). Ungerer and Thomas (1996) reported that concentrations of *o,p′*-DDT were positively correlated with gonadosomatic index in Atlantic croaker (*Micropogonias undulatus*). Juvenile rainbow trout (*Oncorhynchus mykiss*) injected with 45–90 μg g^{-1} *o,p′*-DDE and *o,p′*-DDT had increased plasma vitellogenin concentrations (Donohoe and Curtis, 1996); however, these concentrations of DDTs may not be considered environmentally relevant. Gonadosomatic index was significantly lower in adult female and male Japanese medaka (*Oryzias latipes*) when they had been exposed in ovo to 500 ng g^{-1} *o,p′*-DDE (Papoulias et al., 2003). Metcalfe et al. (2000) suggested that continuous exposure to endocrine active compounds such as *o,p′*-DDT must begin in ovo and continue throughout early development to affect reproductive endpoints in fish. This type of exposure to DDT may be particularly relevant for fish from McIntosh. Fish spawning in the spring may be exposed to *o,p′*-isomers if they migrate and consume prey in the contaminated floodplain during high flows. Studies have also reported that *o,p′*-isomers can affect immune responses and behavior in fish. For example, Chinook salmon (*Oncorhynchus tshawytscha*) eggs immersed in 10 μg g^{-1} *o,p′*-DDE may have increased susceptibility to disease because of a reduction in splenic leukocyte blastogenesis (Milston et al., 2003). Visual and vibratory stimuli responses and routine swimming activity were impaired in Atlantic croaker larvae exposed to *o,p′*-DDT, which may decrease survival by increasing predation, decreasing feeding rates, or both (Faulk et al., 1999).

Reduced reproductive success of bald eagle and osprey populations has been associated with exposure to organochlorine pesticides including *p,p′*-DDE. Specifically, eggshell thinning is one of the main effects of *p,p′*-DDE exposure in bald eagle and osprey, which has resulted in substantial population-level effects (Anderson and Hickey, 1972; Wiemeyer et al., 1984, 1988). For example, osprey from various U.S. populations with severe eggshell thinning (15–20%) had *p,p′*-DDE egg concentrations of 4200–8700 ng g^{-1} (Wiemeyer et al., 1988). In bald eagle populations, *p,p′*-DDE egg concentrations of 5100–15,000 ng g^{-1} were associated with decreased young production (Wiemeyer et al., 1984; Krantz et al., 1970). Although a variety of piscivorous birds occur in the lower Mobile River basin, the extent of use and nesting success of piscivorous birds near McIntosh is largely undocumented (P. Tuttle, USFWS, Daphne, Alabama).

The rapid metabolism of *o,p′*-isomers results in low concentrations in birds (Norstrom and Letcher, 1997); however, birds can be exposed to *o,p′*-isomers through their regular consumption of prey, including fish, with high DDT concentrations. Potential estrogenic effects of *o,p′*-isomers to birds are not well studied. Fry and Toone (1981) reported oviduct formation in male California gull (*Larus californicus*) exposed in ovo to 5 μg g^{-1} *o,p′*-DDT. Higher concentrations of *o,p′*-DDT (150 μg g^{-1}) in female Japanese quail (*Coturnix japonica*) eggs caused oviduct abnormalities and egg laying impairment (Halldin, 2005). Toxicity reference values for *o,p′*-DDE, *o,p′*-DDD, and *o,p′*-DDT need to be developed to better understand the risk these compounds pose to fish and wildlife.

3.4.2. Chlorinated benzenes

Concentrations of hexachlorobenzene were compared to thresholds to protect piscivorous wildlife; thresholds were not available for pentachlorobenzene. Hexachlorobenzene is less toxic to fish than many other persistent organochlorines but may contain

toxic impurities including polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (Schmitt et al., 1999). Hexachlorobenzene is a known porphyrinogen and is toxic to bird embryos (Boersma et al., 1986). Hexachlorobenzene embryotoxicity was thought to be responsible for the complete failure of herring gull eggs to hatch in Lake Ontario in the early 1970s (Norstrom, 2006). Based on data from Boersma et al. (1986) and Braune and Norstrom (1989), whole-fish concentrations of hexachlorobenzene that range from 48 to 161 ng g^{-1} may cause reproductive failure in herring gull eggs. Herring gull is one of the more resistant species to organohalogen contaminants such as PCBs and TCDD (Norstrom, 2006); therefore, the threshold for other species, such as bald eagle and osprey, may be lower than 48 ng g^{-1}. Hexachlorobenzene concentrations >330 ng g^{-1} in whole-fish may represent a risk to piscivorous wildlife (Newell et al., 1987). Bass from Childersburg, Eureka Landing, Lavaca, and Bucks did not exceed the thresholds for hexachlorobenzene (Fig. 6). In contrast, hexachlorobenzene concentrations in McIntosh bass were 12–1100 ng g^{-1}, with six of ten bass exceeding at least one threshold to protect avian embryos (Fig. 6). Of these six bass, four (all male) had hexachlorobenzene concentrations >200 ng g^{-1}. Given the high hexachlorobenzene concentrations in bass from McIntosh, the reproductive success of piscivorous birds foraging on bass in this area may be compromised.

3.4.3. Toxaphene

Although generally considered non-toxic to birds, toxaphene is highly toxic to fish (Wiemeyer, 1996; Jarvinen and Ankley, 1999). Freshwater fish with toxaphene concentrations of 203 ng g^{-1} produced eggs with reduced viability (Mayer et al., 1975). Bass from Childersburg, Eureka Landing, Lavaca, and Bucks did not exceed the threshold for toxaphene, but two of ten bass from McIntosh did (Fig. 6).

3.4.4. Total PCBs

Concentrations of total PCBs were compared to thresholds to protect fish and wildlife. Inferior reproductive performance and offspring survival were reported in American mink, one of the most sensitive species to PCBs, that were fed fish or fish products with PCB concentrations of 480 ng g^{-1} (Hornshaw et al., 1983). Eisler (1986) proposed thresholds for total PCB concentrations of 400 ng g^{-1} in whole-body fish to avoid reproductive impairment and 3000 ng g^{-1} to protect birds. Total PCB concentrations in Childersburg ($n = 2$) and McIntosh ($n = 5$) bass exceeded thresholds to protect fish and mink; concentrations in bass from Eureka Landing, Lavaca, and Bucks did not exceed these thresholds (Fig. 6). Concentrations in all samples were less than the threshold to protect birds (Fig. 6).

4. Conclusions

Although DDT has not been produced at the McIntosh manufacturing facility since 1963, the site continues to release DDT into the adjacent river. Mean concentrations of *o*,*p*′- and *p*,*p*′-DDT isomers in bass at McIntosh were significantly greater than those from four other sites in the Mobile River basin. Proportions of *o*,*p*′- versus *p*,*p*′-isomers were greater in bass at McIntosh compared to other sites and were consistent with *o*,*p*′-isomer ratios in sediments and tar cake from a DDT manufacturing acid waste site. Concentrations of *o*,*p*′-isomers, which are endocrine active, were high in McIntosh bass, but the reproductive health of bass at McIntosh is unknown. Mean total DDT concentrations in bass from McIntosh were at least four times greater than bass from all sites of a contemporary U.S. monitoring program. Comparison of historical DDT concentrations to those in the present study revealed that *p*,*p*′-DDE, *p*,*p*′-DDD, and *p*,*p*′-DDT concentrations have not declined in

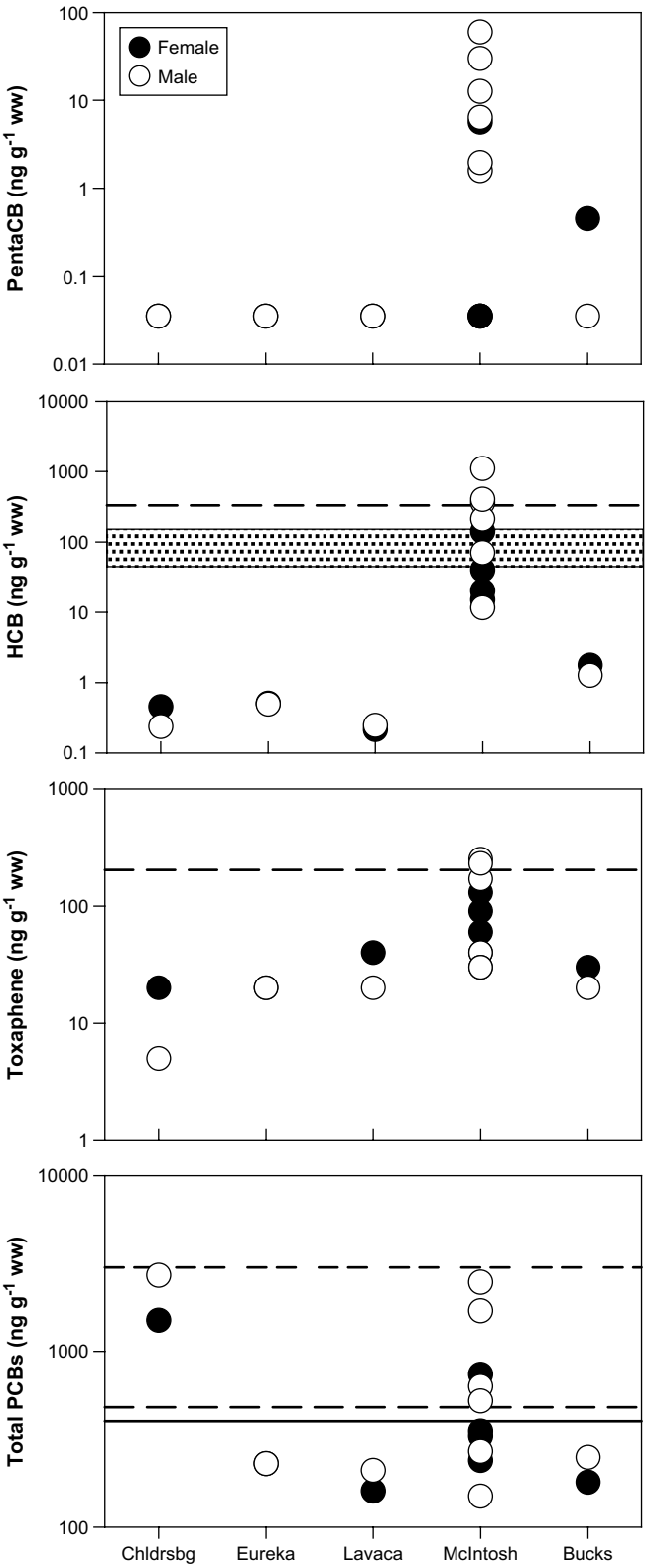

Fig. 6. Concentrations of pentachlorobenzene (pentaCB), hexachlorobenzene (HCB), toxaphene, and total PCBs in largemouth bass. The reference lines on the HCB graph represent protective thresholds for piscivorous wildlife (330 ng g^{-1}; Newell et al., 1987) and herring gull embryos (48–161 ng g^{-1}; Boersma et al., 1986; Braune and Norstrom, 1989). On the toxaphene graph, whole-body concentrations greater than 203 ng g^{-1} have caused reduced egg viability in fish (Mayer et al., 1975). The reference line on the total PCB graph represents the protective thresholds for fish (400 ng g^{-1}; Eisler, 1986), mink (480 ng g^{-1}; Hornshaw et al., 1983), and birds (3000 ng g^{-1}; Eisler, 1986).

bass at McIntosh in the past 20 years, which indicates that fish continue to be exposed to DDT at this site. DDT in bass is persistent and remains at concentrations sufficient to pose a risk to fish and piscivorous birds foraging or nesting near McIntosh.

Pentachlorobenzene, hexachlorobenzene, and toxaphene in bass at McIntosh were also significantly greater than those from other Mobile River basin sites. PCB concentrations in McIntosh bass were greater than those from all other sites except Childersburg. Hexachlorobenzene, toxaphene, and total PCB concentrations exceeded thresholds to protect fish, piscivorous wildlife, or both in bass at McIntosh. Therefore, these contaminants could further compromise the health of fish and piscivorous birds foraging near McIntosh.

Acknowledgements

Data from Childersburg, Eureka Landing, Lavaca, and Buck were from the Large River Monitoring Network of the Biomonitoring Environmental Status and Trends (BEST) Program, which was managed by the Status and Trends Program of the U.S. Geological Survey. K. Chojnacki provided the map. S. Finger, M. Gielazyn, D. Hahn, and P. Tuttle provided useful comments on earlier versions of this paper. J. Coyle, A. Donahue, S. Floyd, A. Ford, R. Lipkin, and P. Tuttle assisted in field collections. J. Meadows, G. Tegerdine, R. Gale, and K. Echols participated in the chemical analysis.

References

American Fisheries Society, American Institute of Fishery Research Biologists, American Society of Ichthyologists and Herpetologists, 2004. Guidelines for the Use of Fishes in Research. American Fisheries Society, Bethesda, Maryland. 54 pp.

Anderson, D.W., Hickey, J.J., 1972. Eggshell changes in certain North American birds. Proc. Int. Ornithol. Congr. 15, 514–540.

Aulerich, R.J., Ringer, R.K., 1977. Current status of PCB toxicity to mink, and effect on their reproduction. Arch. Environ. Contam. Toxicol. 6, 279–292.

Barber, D.S., McNally, A.J., Garcia-Reyero, N., Denslow, N.D., 2007. Exposure to *p,p′*-DDE or dieldrin during the reproductive season alters hepatic CYP expression in largemouth bass (*Micropterus salmoides*). Aquat. Toxicol. 81, 27–35.

Beckvar, N., Dillion, T.M., Read, L.B., 2005. Approaches for linking whole-body fish tissue residues of mercury and DDT to biological effects thresholds. Environ. Toxicol. Chem. 24, 2094–2105.

Boersma, D.C., Ellenton, J.A., Yagminas, A., 1986. Investigation of the hepatic mixed-function oxidase system in herring gull embryos in relation to environmental contaminants. Environ. Toxicol. Chem. 5, 309–318.

Braune, B.M., Norstrom, R.J., 1989. Dynamics of organochlorine compounds in herring gulls: III. Tissue distribution and bioaccumulation in Lake Ontario gulls. Environ. Toxicol. Chem. 8, 957–968.

Buser, H.R., Müller, M.D., 1995. Isomer-selective and enantiomerselective determination of DDT and related-compounds using chiral high-resolution gas-chromatography mass-spectrometry and chiral high-performance liquid-chromatography. Anal. Chem. 67, 2691–2698.

Ciba–Geigy Corporation, 1994. Remedial Investigation/Feasibility Study, Remedial Investigation Addendum, Ecological Assessment of the Floodplain for Ciba-Geigy Corporation, McIntosh, Alabama. Ciba-Geigy Corporation, McIntosh, Alabama. 7 numbered sections plus appendices.

Donohoe, R.E., Curtis, L.R., 1996. Estrogenic activity of chlordecone, *o,p′*-DDT and *o,p′*-DDE in juvenile rainbow trout: induction of vitellogenesis and interaction with hepatic estrogen binding sites. Aquat. Toxicol. 36, 31–52.

Eisler, R., 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: a synoptic review. Biological Reports 85 (1.7). Patuxent Wildlife Research Center, Laurel, Maryland, 53 pp.

Elliott, J.E., Harris, M.L., 2001. An ecotoxicological assessment of chlorinated hydrocarbon effects on bald eagle populations. Rev. Toxicol. 4, 1–60.

Faulk, C.K., Fuiman, L.A., Thomas, P., 1999. Parental exposure to *ortho,para*-dichlorodiphenyltrichloroethane impairs survival skills of Atlantic croaker (*Micropogonias undulatus*) larvae. Environ. Toxicol. Chem. 18, 254–262.

Fry, D.M., Toone, C.K., 1981. DDT-induced feminization of gull embryos. Science 213, 922–924.

Garcia-Reyero, N., Barber, D.S., Gross, T.S., Johnson, K.G., Sepulveda, M.S., Szabo, N.J., Denslow, N.D., 2006. Dietary exposure of largemouth bass to OCPs changes expression of genes important for reproduction. Aquat. Toxicol. 78, 358–369.

Giesy, J.P., Bowerman, W.W., Mora, M.A., Verbrugge, D.A., Othoudt, R.A., Newsed, J.L., Summer, C.L., Aulerich, R.J., Bursian, S.J., Ludwig, J.P., Dawson, G.A., Kubiak, T.J., Best, D.A., Tillitt, D.E., 1995. Contaminants in fishes from Great Lakes-influenced sections and above dams of three Michigan Rivers: III. Implications for health of bald eagles. Arch. Environ. Contam. Toxicol. 29, 309–321.

Glaser, D., Connolly, J.P., 2002. A model of *p,p′*-DDE and total PCB bioaccumulation in birds from the Southern California Bight. Cont. Shelf Res. 22, 1079–1100.

Halldin, K., 2005. Impact of endocrine disrupting chemicals on reproduction in Japanese quail. Domest. Animal Endocrin. 29, 420–429.

Henny, C.J., Kaiser, J.L., Grove, R.A., Bentley, V.R., Elliott, J.E., 2003. Biomagnification factors (fish to osprey eggs from Willamette River, Oregon, U.S.A.) for PCDDs, PCDFs, PCBs and OC pesticides. Environ. Monit. Assess. 84, 275–315.

Hinck, J.E., Schmitt, C.J., Echols, K.R., May, T.W., Orazio, C.E., Tillitt, D.E., 2006. Environmental contaminants in fish and their associated risk to piscivorous wildlife in the Yukon River Basin, Alaska. Arch. Environ. Contam. Toxicol. 51, 661–672.

Hinck, J.E., Blazer, V.S., Denslow, N.D., Echols, K.R., Gross, T.S., May, T.W., Anderson, P.J., Coyle, J.J., Tillitt, D.E., 2007. Chemical contaminants, health indicators, and reproductive biomarker responses in fish from the Colorado River and its tributaries. Sci. Total Environ. 378, 376–402.

Hinck, J.E., Blazer, V.S., Denslow, N.D., Echols, K.R., Gale, R.W., Wieser, C., May, T.W., Ellersieck, M., Coyle, J.J., Tillitt, D.E., 2008. Chemical contaminants, health indicators, and reproductive biomarker responses in fish from rivers in the Southeastern U.S. Sci. Total Environ. 390, 538–557.

Hornshaw, T.C., Aulerich, R.J., Johnson, H.E., 1983. Feeding great lakes fish to mink: effects on mink and accumulation and elimination of PCBs by mink. J. Toxicol. Environ. Health 11, 933–946.

Jarvinen, A.W., Ankley, G.T., 1999. Linkage of Effects to Tissue Residues: Development of a Comprehensive Database for Aquatic Organisms Exposed to Inorganic and Organic Chemicals. Society of Environmental Toxicology and Chemistry (SETAC) Press, Pensacola, Florida, 364 pp.

Keith, L.H., 1991. Environmental Sampling and Analysis. Lewis Publishers, Boca Raton, Florida.

Krantz, W.C., Mulhern, B.M., Bagley, G.E., Sprunt, A.I.V., Ligas, F.J., Roberston Jr., W.B., 1970. Organochlorine and heavy metal residues in bald eagle eggs. Pestic. Monit. J. 4, 136–140.

Looser, R., Froescheis, O., Cailliet, G.M., Jarman, W.M., Ballschmiter, K., 2000. The deep-sea as a final global sink of semivolatile persistent organic pollutants? Part II: organochlorine pesticides in surface and deep-sea dwelling fish of the North and South Atlantic and the Monterey Bay Canyon (California). Chemosphere 40, 661–670.

Mayer Jr., F.L., Mehrle Jr., P.M., Dwyer, W.P., 1975. Toxaphene effects on reproduction, growth, and mortality of brook trout, Duluth, Minnesota. U.S. Environmental Protection Agency Report EPA-600/3-75/013.

Metcalfe, T.L., Metcalfe, C.D., Kiparissis, Y., Niimi, A.J., Foran, C.M., Benson, W.H., 2000. Gonadal development and endocrine responses in Japanese medaka (*Oryzias latipes*) exposed to *o,p′*-DDT in water or through maternal transfer. Environ. Toxicol. Chem. 19, 1893–1900.

Milston, R.H., Fitzpatrick, M.S., Vella, A.T., Clements, S., Gundersen, D., Feist, G., Crippen, T.L., Leong, J., Schreck, C.B., 2003. Short-term exposure of Chinook salmon (*Oncorhynchus tshawytscha*) to *o,p′*-DDE or DMSO during early life-history stages causes long-term humoral immunosuppression. Environ. Health Perspect. 111, 1601–1607.

Newell, A.J., Johnson, D.W., Allen, L.K., 1987. Niagara River Biota Contamination Project: Fish Flesh Criteria for Piscivorous Wildlife. New York State Department of Environmental Conservation, Division of Fish and Wildlife, Bureau of Environmental Protection Technical Report 87-3, 182 pp.

Norstrom, R.J., 2006. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Great Lakes. In: Hites, R.A. (Ed.), Persistent Organic Pollutants in the Great Lakes. Springer-Verlag, Berlin, Germany, pp. 71–150.

Norstrom, R.J., Clark, T.P., Enright, M., Leung, B., Drouillard, K.G., MacDonald, C.R., 2007. ABAM, a model for bioaccumulation of POPs in birds: validation for adult herring gulls and their eggs in Lake Ontario. Environ. Sci. Technol. 41, 4339–4347.

Norstrom, R.J., Letcher, R.J., 1997. Role of biotransformation in bioconcentration and bioaccumulation. In: Sijm, D., deBruin, J., de Voogt, P., de Wolf, P. (Eds.), Biotransformation in Environmental Risk Assessment, Annex 1, Society of Environmental Toxicology and Chemistry (SETAC) – Europe Workshop. SETAC-Europe Pub., Brussels, Belgium, pp. 103–113.

Papoulias, D.M., Villalobos, S.A., Meadows, J., Noltie, D.B., Giesy, J.P., Tillitt, D.E., 2003. In ovo exposure to *o,p′*-DDE affects sexual development but not sexual differentiation in Japanese medaka (*Oryzias latipes*). Environ. Health Perspect. 111, 29–32.

Schmitt, C.J., 1981. Analysis of variance as a method for examining contaminant residues in fish: National Pesticide Monitoring Program. In: American Society for Testing and Materials Special Technical Publication, pp. 270–298.

Schmitt, C.J., 2002. Organochlorine chemical residues in fish from the Mississippi River Basin, 1995. Arch. Environ. Contam. Toxicol. 43, 81–97.

Schmitt, C.J., Zajicek, J.L., May, T.W., Cowman, D.F., 1999. National contaminant biomonitoring program: concentrations of organochlorine chemical residues and elemental contaminants in U.S. freshwater fish, 1976–1986. Rev. Environ. Contam. Toxicol. 162, 43–104.

Schmitt, C.J., Hinck, J.E., Blazer, V.S., Denslow, N.D., Dethloff, G.M., Bartish, T.M., Coyle, J.J., Tillitt, D.E., 2005. Environmental contaminants and biomarker responses in fish from the Rio Grande and its U.S. tributaries: spatial and temporal trends. Sci. Total Environ. 350, 161–193.

Ungerer, J.R., Thomas, P., 1996. Role of very low density lipoproteins in the accumulation of *o,p′*-DDT in fish ovaries during gonadal recrudescence. Aquat. Toxicol. 35, 183–195.

U.S. Environmental Protection Agency, 1995. EPA Superfund Record of Decision: Ciba-Geigy Corp (McIntosh Plant), EPA/ROD/R04-95/244/1995, Atlanta, Georgia, 71 pp.

U.S. Environmental Protection Agency, 2006. Second Five-year Review Report for Ciba-Geigy Chemical Superfund Site, McIntosh, Washington County, Alabama, Athens, Georgia, 77 pp.
U.S. Fish and Wildlife Service, 1989. An Evaluation of Organochlorine Pesticide Contamination in the Tombigbee River near an Industry with a History of DDT Discharges. U.S. Fish and Wildlife Enhancement Report 06-188-00-00-A, 13 pp.
U.S. Fish and Wildlife Service, 1992. An Evaluation of Mercury and DDT Contamination in Fish and Sediments Collected from the Tombigbee River near McIntosh, Alabama. U.S. Fish and Wildlife Enhancement Report 06-192-07-00-A, 46 pp.
U.S. Fish and Wildlife Service, 1996. An Investigation into the Uptake of Contaminants in Largemouth Bass and Sediment from the Lower Tombigbee and Mobile Rivers. U.S. Fish and Wildlife Ecological Services Office Report 06-196-03-00-A, 83 pp.
Venkatesan, M.I., Greene, G.E., Ruth, E., Chartrand, A.B., 1996. DDTs and dumpsite in the Santa Monica Basin, California. Sci. Total Environ. 179, 61–71.
Wiemeyer, S.N., 1996. Other organochlorine pesticides in birds. In: Beyer, W.N., Heinz, G.H., Redmon-Norwood, A.W. (Eds.), Environmental Contaminants in Wildlife-interpreting Tissue Concentrations. Lewis Publishers, Boca Raton, Florida, pp. 99–116.
Wiemeyer, S.N., Lamont, T.G., Bunck, C.M., Sindelar, C.R., Gramlich, F.J., Fraser, J.D., Byrd, M.A., 1984. Organochlorine pesticides, polychlorinated biphenyls, and mercury residues in bald eagle eggs – 1969–79 – and their relationships to shell thinning and reproduction. Arch. Environ. Contam. Toxicol. 13, 529–549.
Wiemeyer, S.N., Bunck, C.M., Krynitsky, A.J., 1988. Organochlorine pesticides, polychlorinated biphenyls, and mercury in osprey eggs – 1970–79 – and their relationships to shell thinning and productivity. Arch. Environ. Contam. Toxicol. 17, 767–787.
Williams, J.B., Siegfreid, W.R., Milton, S.J., Adams, N.J., Dean, W.R.J., Duplessis, M.A., Jackson, S., Nagy, K.A., 1993. Field metabolism, water requirements, and foraging behavior of wild ostriches in the Namib. Ecology 74, 390–404.
Woodward-Clyde, 1994. Additional Ecological Studies for OU-2 McIntosh Plant Site, Olin Corporation, McIntosh, Alabama. Woodward-Clyde Consultants, Baton Rouge, Louisiana. 8 numbered sections plus appendices.