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Abstract. Fish were collected in late 1995 from 34 National Contaminant Biomonitoring Program (NCBP) stations and 13 National Water Quality Assessment Program (NAWQA) stations in the Mississippi River basin (MRB) and in late 1996 from a reference site in West Virginia. Four composite samples, each comprising (nominally) 10 adult common carp (*Cyprinus carpio*) or black bass (*Micropterus* spp.) of the same sex, were collected from each site and analyzed for organochlorine chemical residues by gas chromatography with electron capture detection. At the NCBP stations, which are located on relatively large rivers, concentrations of organochlorine chemical residues were generally lower than when last sampled in the mid-1980s. Residues derived from DDT (primarily *p,p′*-DDE) were detected at all sites (including the reference site); however, only traces ($\leq$ 0.02 μg/g) of the parent insecticide (*p,p′*-DDT) were present, which indicates continued weathering of residual DDT from past use. Nevertheless, concentrations of DDT (as *p,p′*-DDE) in fish from the cotton-farming regions of the lower MRB were great enough to constitute a hazard to fish-eating wildlife and were especially high at the NAWQA sites on the lower-order rivers and streams of the Mississippi embayment. Mirex was detected at only two sites, both in Louisiana, and toxaphene was found exclusively in the lower MRB. Most cyclodiene pesticides (dieldrin, chlordane, and heptachlor epoxide) were more widespread in their distributions, but concentrations were lower than in the 1980s except at a site on the Mississippi River near Memphis, TN. Concentrations were also somewhat elevated at sites in the Corn Belt. Endrin was detected exclusively at the Memphis site. PCB concentrations generally declined, and residues were detected ($\geq$ 0.05 μg/g) at only 35% of the stations, mostly in the more industrialized parts of the MRB.

Environmental concentrations of organochlorine pesticides, polychlorinated biphenyls (PCBs), and other persistent environmental contaminants have generally declined over the last two decades (Schmitt and Bunck 1995; Schmitt *et al.* 1999c; Gundersen *et al.* 2000). In North America and elsewhere the release of many such contaminants to the environment has been reduced or eliminated through regulation and replacement by shorter-lived, less toxic compounds. Nevertheless, there is a substantial body of information indicating that concentrations of accumulative contaminants in fish may remain sufficiently elevated to harm fish and wildlife in some areas (*e.g.*, Gooch and Matsamura 1987; Colborn 1991; Tillitt *et al.* 1992; Schmitt *et al.* 1999c), and concentrations of some contaminants may be increasing in the Arctic (*e.g.*, Muir *et al.* 1999). In addition to continuing incidents of wildlife mortality attributable to persistent, obsolete pesticides (*e.g.*, Stansley and Roscoe 1999), reports of reproductive impairment (see reviews by Colborn *et al.* [1993] and Sumpter *et al.* [1996]), immune system dysfunction (Blazer and Dethloff 2000), and other health problems in fish and wildlife has maintained interest in organochlorine chemicals. Accordingly, concentrations of accumulative contaminants in fish has been proposed as an indicator of sustainable economic development (CEQ 1997), and periodic measurement of these concentrations is an integral part of many environmental monitoring programs (Hirsch *et al.* 1988; Messer *et al.* 1991; BEST 1996; Wong *et al.* 2000).

This article summarizes one component of a larger investigation conducted in 1995–96 (Schmitt and Dethloff 2000) that included both chemical and biological components. The report is intended to provide contemporary information on the distribution, concentrations, and ecological risks of organochlorine chemical residues in fish of the Mississippi River basin (MRB), where contaminants in fish had not been evaluated comprehensively since the mid-1980s (Schmitt *et al.* 1999c). The 1995 results are compared with other contemporary studies and with previous NCBP findings and are evaluated relative to extant information on ecological risk. The larger study was a pilot for a national monitoring program incorporating biological and chemical indicators (Schmitt *et al.* 1999a, 1999b). In addition to the results reported here the study included measurement of elemental contaminant concentrations and biomarkers of chemical exposure and their effects. The overall approach being evaluated was the use of readily available and comparatively inexpensive methods as a first-tier screen, with costlier, higher-resolution methods reserved for follow-up investigations based on tier 1 results. In addition to cost-effectiveness and compatibility with the biological endpoints of the larger investigation (Schmitt *et al.* 1999a; Schmitt and Dethloff 2000), analytical methods were also chosen because of their similarity to those used in the past (Schmitt *et al.* 1999c) for evaluating temporal

trends. Raw data for the entire study, as well as 1969–1986 NCBP data, may be obtained online at *www.cerc.usgs.gov/data/data.htm*.

Materials and Methods

Study Area and Collection Sites

The MRB drains all or parts of 32 states (about 41% of the conterminous United States) and parts of two Canadian provinces (Figure 1) and has a human population of more than 72 million. Agricultural development in the MRB is extensive, accounting for > 50% of U.S. corn, wheat, soybean, cattle, and hog production (Goolsby 1996). There is also substantial urban, industrial, and mining development. Consequently, many programs and studies (*e.g.*, Thurman *et al.* 1991; Goolsby *et al.* 1993; Ellis *et al.* 1995; Meade 1995; Schmitt *et al.* 1999c; Wong *et al.* 2000) have documented the presence and widespread distribution of numerous contaminants of agricultural, industrial, and mining origin in the Mississippi River and its tributaries, as well as the export of nutrients and contaminants to the Gulf of Mexico (Trefry *et al.* 1985; Meade 1995; Rostad 1997). Information on contaminants in the large rivers of the MRB needed to be updated because substantial quantities of pesticides and other materials were redistributed and transported out of the basin by extreme flooding in 1993 and 1995 (Rostad 1997).

Fish were collected in late 1995 from 34 of the 38 National Contaminant Biomonitoring Program (NCBP) stations in the MRB (Figure 1, Table 1) and analyzed for organochlorine chemical residues (Table 2). Two NCBP sites in the upper Platte River system were not sampled because organochlorine chemicals had been extensively investigated there in 1992–93 (Tate and Heiny 1996). At the NCBP stations, which represent key points (*i.e.*, confluences of major tributaries, impoundments) on some of the largest U.S. rivers, concentrations of accumulative contaminants in fish were monitored from 1967 through 1986 (Johnson *et al.* 1967; Schmitt and Bunck 1995; Schmitt *et al.* 1999c). Fish were also collected in 1995 at 13 National Water Quality Assessment Program (NAWQA) sites—9 in the Mississippi Embayment (MSE) Study Unit (Mallory 1994) and 4 in the Eastern Iowa Basins (EIB) Study Unit (Kalkhoff *et al.* 1994; Figure 1, Table 1). The NAWQA sites typically represent lower-order rives and streams than the NCBP sites. Because all the NCBP and NAWQA sites in the MRB are contaminated to some degree, samples were also collected in late 1996 from the water supply reservoirs of the USGS Leetown Science Center in Kearneysville, WV (reference site) to better document contemporary background conditions.

Field Procedures

Fish were captured by electrofishing and held alive until needed for processing (generally < 4 h). At each NCBP site, a total of 40 adult fish representing two taxa—common carp (*Cyprinus carpio*, hereafter "carp") and black basses (*Micropterus* spp., "bass")—were sought, with the target being 10 males and 10 females of each species. Alternate bottom-dwelling and piscivorous species were permitted as necessary. At the NAWQA stations only carp (10 males, 10 females) were collected at 11 sites, only largemouth bass (*M. salmoides*) were collected at 1 site, and both species were collected at 1 site. These taxa were selected because they had been prevalent in past NCBP and NAWQA collections (Crawford and Luoma 1992; Schmitt *et al.* 1999c) and because the biological endpoints measured in other components of the study had been most thoroughly tested in them (Schmitt *et al.* 1999b; Schmitt and Dethloff 2000). Fish were processed as described by Schmitt *et al.* (1999b). In short, each fish was measured, weighed, and placed on a clean sheet of aluminum foil. The abdominal cavity was dissected open and gender was determined by gonadal observation. Samples of blood, liver, kidney, scales, and spleen were obtained for other analyses (Schmitt *et al.* 1999a). After processing, all remaining tissues were returned to the carcass, which was wrapped in the foil on which it was processed, labeled, and chilled. Carcass samples comprised whole fish minus approximately 5 ml of blood, five to eight 1-cm^3 pieces of liver, five 1–cm^3 gonad pieces, the entire spleen, 5–10 scales, and a 1-cm^3 piece of both the posterior and anterior kidneys. The total mass of tissues not included in the carcass analyses represented < 1% of the original mass of each fish. Between samples all contact surfaces and instruments were thoroughly cleaned with tap water and rinsed with deionized water and acetone. After all sampling at a station was completed, fish were frozen (−20°C) and shipped to the analytical laboratory, where they were kept frozen until prepared for analysis.

Laboratory Analyses

Chemical analyses were performed by contract laboratories under the supervision of the U.S. Fish and Wildlife Service (FWS) Patuxent Analytical Control Facility (PACF) in Laurel, MD, which maintained quality assurance (Q/A) oversight. For compatibility with other aspects of the larger study (Schmitt *et al.* 1999a; Schmitt and Dethloff 2000), samples from each station were composited by species and gender. Individual fish were first band-sawed into pieces after which all the pieces of all the fish in the sample being prepared were ground together three times with a commercial meat grinder. A 10-g subsample was retained for gravimetric determination of lipid content and analysis of organochlorine chemical residues by gas chromatography with electron capture detection (GC-ECD). Additional aliquots were retained for Q/A and for analyses not reported here. Between samples all equipment was disassembled, washed in hot soapy water, and rinsed with water, acetone, and petroleum ether. The 10-g subsamples of ground fish were mixed with anhydrous sodium sulfate, Soxhlet-extracted with hexane for 7 h, and concentrated by rotary evaporation. The concentrated samples were transferred to tared test tubes and evaporated to constant weight to estimate lipid content. After weighing, the lipid samples were redissolved in 12 ml petroleum ether (in three washes of 5, 4, and 3 ml), then extracted four times with 30 ml (each) of acetonitrile saturated with petroleum ether. Residues in this extract were partitioned into petroleum ether, concentrated to 4–5 ml by Kuderna-Danish, and transferred to glass chromatographic columns containing 20 g of Florisil®. The Florisil was eluted with 200 ml 6% diethyl ether in petroleum ether (F-I) followed by 200 ml 15% diethyl ether in petroleum ether (F-II). Both fractions were concentrated to 10 ml. F-II was analyzed for polar insecticide residues by dual megabore-column GC-ECD. F-I was transferred to a glass column (40 mm × 1 cm ID with a 14- × 4-cm ID reservoir on top) containing 5 g of silicic acid (Mallinckrodt 7068, activated at 130°C for ≥ 7 days), from which three fractions were eluted: SA-I (20 ml of petroleum ether) contained hexachlorobenzene (HCB) and mirex; SA-II (150 ml of petroleum ether) contained PCBs; and SA-III (20 ml of 1:19:80 acetonitrile: hexane:methylene chloride) contained organochlorine pesticides. Each of these fractions was concentrated to 10 ml for megabore-column GC-ECD using dual DB-608 and DB-5 (30-m × 0.52-mm ID) columns, with the injection split between the columns and routed to two detectors. Temperatures were injector, 220°C; detector, 300°C; and column, 160°C for 5 min, increased 2°C/min to 210°C for 8 min, then increased 5°C/min, to 230°C for 4 min. The make-up gas was N_2, and the carrier gas was H_2. PCB residues in SA-II were quantified against 1-μl injections of 0.5-ng/μl Aroclor 1242, 1248, 1254, and 1260 standards. Starting with Aroclor 1260, four peaks unique to this mixture were located and their areas summed. The same peaks in

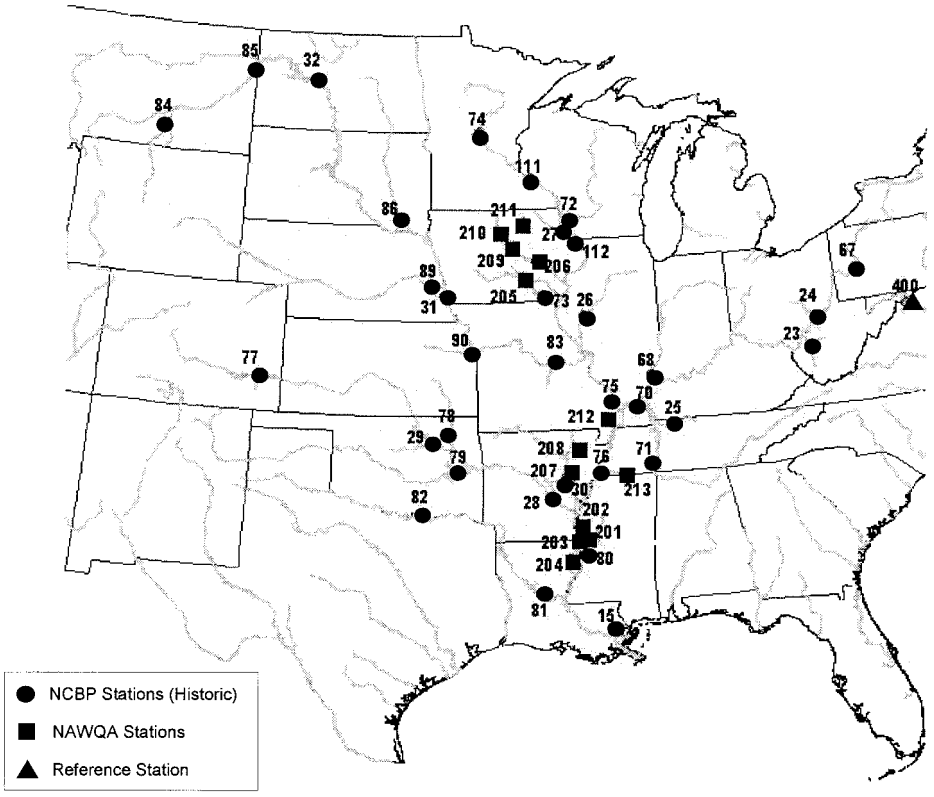

Fig. 1. Map of the central United States showing the Mississippi River Basin (shaded area) and the stations sampled in 1995 (1996 for Station 400). See Table 1 for river names and station locations

the sample were also located and summed, and Aroclor 1260 (in μg/g wet weight) was estimated as [(sample area)(ng 1260 standard)] / [(standard area)(mg sample extracted)]. Aroclor 1254 was also estimated by locating the major peaks (typically four) in the mixture that are normally found in environmental samples. The areas of these peaks were summed, but because some this area also represents Aroclor 1260 the 1260 contribution was subtracted from the total area: [(sample area)–[(μg/g 1260)(mg sample extracted)(area from 1260)(ng 1260 standard)](ng 1254 standard)] / [(area 1254 standard)(mg sample extracted)]. Aroclor 1248 was estimated similarly, after accounting for both 1260 and 1254. Aroclor 1242 was quantified using the area of five early eluting peaks present in the standard. Total PCB was reported as the sum of the four Aroclor mixtures estimated per above. Toxaphene residues in SA-III were quantified using the areas of five to six peaks present in both the samples and standards. The nominal limit of detection (LOD) for individual compounds was 0.01 μg/g wet weight, and for toxaphene and total PCBs it was 0.05 μg/g. As previously (Schmitt *et al.* 1999c), analytical results were not adjusted to reflect spike recoveries or moisture loss during storage

Precision and accuracy of laboratory results were confirmed through analyses of procedural blanks, duplicates, fortified samples, and reference materials. Duplicate analyses (n = 9) typically differed by 3–5% except for total PCBs (9%). Mean recovery efficiency of fortified samples (n = 9) was 92–104% except for dieldrin (88%) and HCB (70%). The identities of residues were confirmed by gas chromatography/mass spectrometry (GC/MS) in about 10% of the samples with a Varian Saturn 2000 ion-trap MS, positive EI mode, on a 30-m × 0.25-mm (ID) DB-5 capillary column and a Model 1078 injector (14 psi head pressure, trap 235°C, manifold 50°C, transfer line 285°C). Injector temperature was 300°C. Column temperatures were 40°C for 2 min; increase 25°C/min to 150°C; increase 4°C/min to 290°C; hold 3.6 min. Round-robin tests among PACF and contract laboratories were also conducted.

Data Set Composition and Statistical Analyses

A total of 164 composite samples from 46 stations (including the reference site) were analyzed. Of these, 89 samples (54%) from 45 stations (96%) were carp and 58 (35%) from 30 stations (64%) were bass—largemouth, smallmouth (*Micropterus dolomieui*), and spotted (*M. punctulatus*). The remaining 17 samples (11%) comprised white suckers (*Catostomus commersoni*; two samples from one station), white bass (*Morone chrysops*; four samples, two stations), sauger (*Stizostedion canadense*; three samples, two stations), brown trout (*Salmo trutta*; two samples, one station), goldeye (*Hiodon alosoides*; two samples, one station), smallmouth buffalo (*Ictiobus bubalus*; two samples, one station), and northern pike (*Esox lucius*; one sample, one station). At most NCBP stations there was at least one species common to both the 1995 and 1986 collections (Schmitt *et al.* 1999c) for the examination of within-taxon temporal trends.

Concentrations of most organochlorine chemical residues were below the LOD in many samples (Table 2), which precluded rigorous statistical analysis. As in the past (Schmitt *et al.* 1999c), a value of one-half the LOD was substituted for the censored values in the computation of unweighted geometric species, sex, and station means, which introduces relatively little bias (US EPA 2000). Because temporal and geographic comparisons are readily confounded by differences among taxa (Schmitt *et al.* 1999c), within-taxon comparisons were made where possible. Only for *p,p′*-DDE were there sufficient numbers of uncensored observations in both carp and bass for statistical testing. For geographic analysis stations were aggregated by subbasin and program (NCBP vs. NAWQA—Table 1). The MSE and EIB Study Units are wholly contained within the Lower Mississippi River and Upper Mississippi River subbasins, respectively (Figure 1, Table 1). Therefore, comparisons of these subbasins represent regional contrasts of large-river stations against those on lower-order rivers and

Table 1. Locations of National Contaminant Biomonitoring Program (NCBP) and National Water Quality Assessment Program (NAWQA) stations in the Mississippi River basin (sampled in 1995) and of the reference site (sampled in 1996)

Program, Subbasin (NCBP) or Study Unit (NAWQA) and Station Number	River	Nearest City or Feature	Latitude (dd-mm-ss)	Longitude (dd-mm-ss)
NCBP				
Arkansas-Red R. (ARR)				
29	Arkansas	Keystone Res., OK	36-07-54.0	96-20-47.0
77	Arkansas	John Martin Res., CO	38-03-55.0	102-56-02.0
78	Verdigris	Oolagah, OK	36-31-16.0	95-33-37.0
79	Canadian	Eufaula, OK	35-16-43.0	95-34-39.0
82	Red	Lake Texoma, TX/OK	33-52-08.0	96-47-04.0
Lower Missouri R. (LMO)				
31	Missouri	Nebraska City, NE	40-40-15.9	95-49-44.6
83	Missouri	Hermann, MO	38-42-24.1	91-26-17.5
86	James	Olivet, SD	43-13-45.0	97-41-05.0
89	Platte	Louisville, NE	40-59-33.1	96-12-30.9
90	Kansas	Bonner Springs, KS	39-02-47.0	94-47-05.0
Upper Missouri R. (UMO)				
32	Missouri	Garrison Dam, ND	47-28-27.3	101-26-15.5
84	Big Horn	Hardin, MT	45-52-12.2	107-34-34.0
85	Yellowstone	Sidney, NE	47-34-46.8	104-13-10.7
Lower Mississippi R. (LMR)				
15	Mississippi	Luling, LA	29-59-53.2	90-25-31.1
28	Arkansas	Pine Bluff, AR	34-16-27.0	94-57-12.0
30	White	Devall's Bluff, AR	34-47-01.0	91-26-28.0
75	Mississippi	Cape Girardeau, MO	37-18-36.0	89-31-01.2
76	Mississippi	Memphis, TN	38-08-30.3	90-03-36.6
80	Yazoo	Redwood, MS	32-24-36.0	90-55-27.0
81	Red	Alexandria, LA	31-20-48.0	92-27-37.0
Upper Mississippi R. (UMR)				
26	Illinois	Beardstown, IL	40-07-50.6	90-20-45.6
27	Mississippi	Guttenburg, IA	42-43-37.2	91-01-30.0
72	Wisconsin	Woodman, WI	43-05-42.0	90-48-57.6
73	Des Moines	Keosauqua, IA	40-44-52.8	91-59-38.4
74	Mississippi	Little Falls, MN	45-58-48.0	94-22-00.0
111	Mississippi	Lake City, MN	44-22-49.8	92-07-33.0
112	Mississippi	Dubuque, IA	42-26-27.6	90-35-06.0
Ohio R. (OHR)				
23	Kanawha	Winfield, WV	38-29-06.0	81-48-57.6
24	Ohio	Marietta, OH	39-24-36.8	81-26-26.3
25	Cumberland	Clarksville, OH	36-32-28.6	87-22-04.7
67	Allegheny	Natrona, PA	40-39-54.0	79-41-24.0
68	Wabash	New Harmony, IN	38-11-58.4	87-58-36.0
70	Ohio	Metropolis, IL	37-07-40.8	88-39-25.2
71	Tennessee	Savannah, TN	35-12-52.0	88-18-36.0
NAWQA				
Eastern Iowa Basins (EIB)				
205	S. Skunk	Oskaloosa, IA	41-21-19.0	92-39-31.0
206	Iowa	Morengo, IA	41-50-23.0	92-11-54.0
209	S. Fork Iowa	New Providence, IA	42-19-26.0	93-10-10.0
210	Iowa	Rowan, IA	42-45-36.0	93-37-23.0
211	Cedar	St. Charles City, IA	43-03-45.0	92-40-23.0
Mississippi Embayment (MSE)				
201	Big Sunflower	Anguilla, MS	32-58-18.0	90-46-40.0
202	Bogue Phalia	Leland, MS	33-24-22.0	90-50-26.0
203	Steele Bayou	Rolling Fork, MS	32-54-71.0	90-57-10.0
204	Tensas	Tendal, LA	32-25-56.0	91-21-57.0
207	Cache	Cotton Plant, AR	35-02-32.0	91-19-12.0
208	Cache	Egypt, AR	35-51-23.0	90-56-15.0
212	Little R. Ditch	Moorehouse, MO	36-50-03.0	89-43-48.0
213	Wolf	LaGrange, TN	35-01-57.0	89-14-48.0
Reference site				
400	Leetown Res.	Kearneysville, WV	39-21-2.2	77-55-32.69

Table 2. Occurrence (percentages of samples and stations, including the reference site) and limits of detection (LOD) of organochlorine chemical residues in composite samples of whole fish (also shown are maximum concentrations and the sample [station, sex, and species] in which they occurred)

Analyte(s)	Samples (% of 163)	Stations (% of 46)	LOD (μg/g)	Maximum 1995 Concentrations			
				Conc. (μg/g)	Station	Sex	Species
p,p′-DDT[1]	8	15	0.01	0.14	24	F	Common carp
p,p′-DDD (TDE)[2]	58	74	0.01	2.80	201	M	Common carp
p,p′-DDE[3]	91	100	0.01	8.30	201	M	Common carp
Total *p,p′*-homologs	91	100	0.01	11.10	201	M	Common carp
o,p′-DDT[4]	3	4	0.01	0.24	24	F	Common carp
o,p′-DDD (TDE)[5]	12	24	0.01	0.34	24	F	Common carp
o,p′-DDE[6]	1	2	0.01	0.02	24	F	Common carp
Dieldrin[7]	42	57	0.01	0.25	76	F	Common carp
Endrin[8]	2	2	0.01	0.70	76	F	Common carp
cis-Chlordane[9]	37	48	0.01	0.12	76	F	Common carp
trans-Chlordane[10]	9	30	0.01	0.35	76	F	Common carp
cis-Nonachlor[11]	21	35	0.01	0.05	23	F	Smallmouth buffalo
trans-Nonachlor[12]	51	70	0.01	0.31	23	M	Spotted bass
Oxychlordane[13]	6	9	0.01	0.03	76	F	Common carp
Heptachlor epoxide[14]	9	15	0.01	0.08	206	M	Common carp
Total chlordane-related residues[15]	51	70	0.01	0.54	76	F	Common carp
Toxaphene	7	11	0.05	8.3	201	M	Common carp
Mirex[16]	4	4	0.01	0.08	204	M	Common carp
Hexachlorobenzene (HCB)[17]	2	7	0.01	0.07	24	M	Common carp
Total PCBs	21	35	0.05	3.3	24	M	Common carp
Hexachlorocylohexane (HCH)[18]	0	0	0.01	0	—	—	—

See Table 1 for station locations.
ND, not detected.
[1] 2,2-bis (*p*-Chlorophenyl)-1,1,1-trichloroethane
[2] 2,2-bis (*p*-Chlorophenyl)-1,1-dichloroethane
[3] 2,2-bis (*p*-Chlorophenyl)-1,1-dichloroethylene
[4] 2-(*o*-Chlorophenyl)-2-(*p*-chlorophenyl)–1,1,1-trichloroethane
[5] 2-(*o*-Chlorophenyl)-2-(*p*-chlorophenyl)–1,1-dichloroethane
[6] 2-(*o*-Chlorophenyl)-2(*p*-chlorophenyl)–1,1-dichloroethylene
[7] 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
[8] 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
[9] 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene(1-α,2-α,3a-α,4-β,7-β,7a-α)
[10] 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene(1-α,2-β,3a-α,4-β,7-β,7a-α)
[11] 1,2,3,4,5,6,7,8,8-Nonachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene(1-α,2-α,3-α,3a-α,4-β,7-β,7a-α)
[12] 1,2,3,4,5,6,7,8,8-Nonachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene(1-α,2-β,3-α,3a-α,4-β,7-β,7a-α)
[13] 2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno(1,2-b)oxirene(1a-α,1b-β,2-α,5-α,5a-β,6-β,6a-α)
[14] 1,4,5,6,7,8,8-Heptachloro-2,3,-epoxy-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene
[15] Sum of *cis*- and *trans*-chlordanes and nonachlors; oxychlordane; and heptachlor epoxide
[16] 1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachloro-octahydro-1,3,4-metheno-1H-cyclobuta(cd)pentalene
[17] Perchlorobenzene
[18] Sum of α- and γ-hexachlorocyclohexane

streams. Analysis using Levene's test indicated that the log-transformed *p,p′*-DDE concentrations reasonably approximated normality. Transformed concentrations in carp and bass were therefore tested by analysis of variance (ANOVA) using a nested linear model that included terms for subbasin, program, and sex. This analysis revealed small but nevertheless significant ($p < 0.05$) differences between genders for *p,p′*-DDE in carp but not in bass (data not shown). Consequently, four stations (23, 29, 76, and 77) were eliminated from the geographic statistical analysis of *p,p′*-DDE in carp due to either mixed-gender compositing (caused by fish that either could not be identified to sex or were misidentified in the field, as verified by histopathological examination of preserved gonad samples) or the collection of only one gender at the station. Differences among means were compared using Fisher's protected LSD. Temporal changes for *p,p′*-DDE at individual NCBP stations were tested by analyzing the log-transformed concentrations in the 141 station-year-species combinations (total $n = 242$) in the combined-year data set as a one-way ANOVA. Fisher's protected LSD was then used to contrast only the 36 pairs of station-year-species means representing 1995 vs. 1986 concentrations (1984 for Station 90) in the same species at a site. For other compounds the unweighted species (or higher-order taxon) and station-species means at NCBP sites were compared graphically with findings from the most recent NCBP collection (1984 or 1986; data not shown).

Results and Discussion

DDT and Its Primary Metabolites

Prior to 1972 the insecticide DDT (dichlorodiphenyltrichloroethane) was used to control many pests throughout the United States Environmental residues of DDT and its degradation products therefore persist in many areas from historic use, especially in cotton-growing regions (Schmitt *et al.* 1999c). Residues also remain evident near sites of former DDT production and synthesis and as a result of atmospheric transport from parts of the world where DDT is still used. Although long-lived, *p,p′*-DDT, the active insecticide, is metabolized by vertebrates to a number of other residues, the most stable and toxic of which is *p,p′*-DDE. In 1995 (note: here and elsewhere, 1996 for Station 400), DDT residues (as *p,p′*-DDE) were detected in 91% of the samples and at all stations (Figure 2 and 3, Table 2), including the reference site (Figure 2). Total DDT concentrations (sum of *p,p′*-homologs) in individual 1995 samples ranged from nondetectable (< 0.01 μg/g) to 11 μg/g (Table 2). All of the greatest concentrations of total DDT (*i.e.*, ≥ 1.0 μg/g) and of *p,p′*-DDE occurred in the southernmost part of the MRB, at NAWQA Stations 201, 202, 203, and 204 (in the MSE Study Unit) and at NCBP Station 80 (Yazoo R. at Redwood, MS; Figure 2 and 3). These concentrations were about 10-fold greater than those reported by Tate and Heiny (1996) in fish from the South Platte River basin. Total DDT concentrations in fish from Station 400 were 0.3–0.4 μg/g (mostly as *p,p′*-DDE) in carp and < 0.1 μg/g in largemouth bass (Figure 2).

The predominant homolog in all 1995 samples with detectable residues was *p,p′*-DDE (Figure 3). Next most abundant was *p,p′*-DDD, an anaerobic metabolite of *p,p′*-DDT that was also used historically as an insecticide. Traces (< 0.02 μg/g) of *p,p′*-DDT, the parent insecticide, were found in only seven samples—two from each of Stations 80, 24 (Ohio R. at Marietta, OH), and 28 (Arkansas R. at Pine Bluff, AR) and one from Station 67 (Allegheny R. at Natrona, PA). Station 80 has a long history of contamination by DDT and other organochlorine pesticides from cotton farming in the Yazoo River basin, and Station 28 is influenced by a facility at which DDT was synthesized for military use. No *p,p′*-DDT was detected in any sample from the NAWQA sites, including those in the Yazoo basin, despite fivefold greater total DDT concentrations in all samples from Stations 201–204 than at Station 80 (Figure 2). Traces of *o,p′*-DDT homologs, mostly as the degradation product *o,p′*-DDD, were present in at least one sample from the reference site (Station 400); at NCBP Stations 28 (Arkansas R.), 67 (Allegheny R.), 68 (Wabash R. at New Harmony, IN), 80, and 81; and NAWQA Stations 201–204 (all in the MSE Study Unit) and 211 (Cedar R. at St. Charles City, IA; data not shown). Most concentrations were low (< 0.05 μg/g; $\leq 10\%$ of *p,p′*-DDE) and occurred in samples that also contained at least slightly elevated concentrations of *p,p′*-DDE. A notable exception was Station 24 (Ohio R. at Marietta, OH), where *o,p′*-homologs occurred at about the same concentration as *p,p′*-homologs (approximately 0.5–0.6 μg/g) in both carp and bass and where samples also contained traces of *p,p′*-DDT (Table 2). Such high relative concentrations of *o,p′* homologs together with traces of *p,p′*-DDT suggest recently mobilized DDT at this site (Aguillar 1984; Nowell *et al.* 1999).

Among NCBP sites sampled in 1995, total DDT concentrations were greatest at Stations 80 and 81, as they were in 1986 (Schmitt *et al.* 1999c). The mean 1995 total DDT concentration at Station 80 was 1.2 μg/g, mostly as *p,p′*-DDE (Figure 3). In 1986, the Station 80 mean was 2.5 μg/g and included about 0.3 μg/g (12%) of *p,p′*-DDT (Schmitt *et al.* 1999c). Total DDT concentrations also declined, but to a lesser extent, at NCBP Station 81 (Red R. at Alexandria, LA), from a mean of 0.5 μg/g in 1986 to about 0.3 μg/g in 1995. However, it should be noted that there were no taxa in common to both the 1986 and 1995 collections at either of these stations. Nationally, Station 80 historically yielded fish with the greatest concentrations of total DDT; concentrations were 10–30 μg/g in the early 1970s (Schmitt *et al.* 1981) and declined steadily to 2–6 μg/g in 1986 (Schmitt *et al.* 1999c) and < 3 μg/g in 1995. Total DDT concentrations in fish collected in 1995 from NAWQA Stations 201–204 (4–11 μg/g) were comparable to Station 80 concentrations of the late 1970s and early 1980s (Schmitt *et al.* 1983, 1985). Concentrations also declined at most of the stations where within-taxon comparisons could be made. The exceptions were carp and largemouth bass from Station 67 (Allegheny R.) and carp from Station 82 (L. Texoma), in which concentrations increased slightly; however, these increases were only marginally statistically significant (Fisher's protected LSD; $p = 0.08$ for Station 67 carp, $p = 0.15$ for Station 67 bass, and $p = 0.07$ for Station 82 carp). In contrast, *p,p′*-DDE declined significantly ($p < 0.05$) in carp from Stations 25 (Tennessee R.), 29 (Arkansas R.), 70 (Ohio R. at Metropolis, OH), 76 (Mississippi R. at Memphis, TN), 78 (Verdigris R.), 79 (Canadian R.), 85 (Yellowstone R.), 86 (James R.), and 112 (Mississippi R. at Dubuque, IA). No differences in other species were statistically significant ($p > 0.01$).

Residues of DDT (as *p,p′*-DDE) were detected in about 95% of the carp and bass samples analyzed (Table 2). Concentrations differed significantly ($p < 0.01$) among subbasins and between NAWQA and NCBP stations (Table 3). Most subbasins differed significantly ($p < 0.01$) from each other and from the reference site for both carp and bass, but most mean concentrations were low and the differences were small (Table 3). The exception was the MSE Study Unit, where concentrations of *p,p′*-DDE in carp were significantly ($p < 0.01$) greater than in all MRB subbasins, including the Lower Mississippi River (in which the MSE Study Unit is contained). In contrast, *p,p′*-DDE concentrations in EIB carp were significantly ($p < 0.01$) lower than in carp from the Upper Mississippi River subbasin; however, the concentrations were low in both and the differences were small (Table 3). As a group, *p,p′*-DDE concentrations were significantly greater ($p < 0.01$) in carp from the NAWQA sites than from the NCBP sites due to the very high levels in fish from the MSE Study Unit, but only the mean for NCBP sites differed significantly from the reference site where concentrations in carp were very low (Table 3). Concentrations in bass did not differ significantly between NCBP and NAWQA sites (two stations); however, concentrations at the NCBP stations, but not the NAWQA sites, were significantly lower than at the reference site (Table 3).

The proportional composition of the DDT mixture present in U.S. freshwater fish gradually changed after the 1972 U.S. ban.

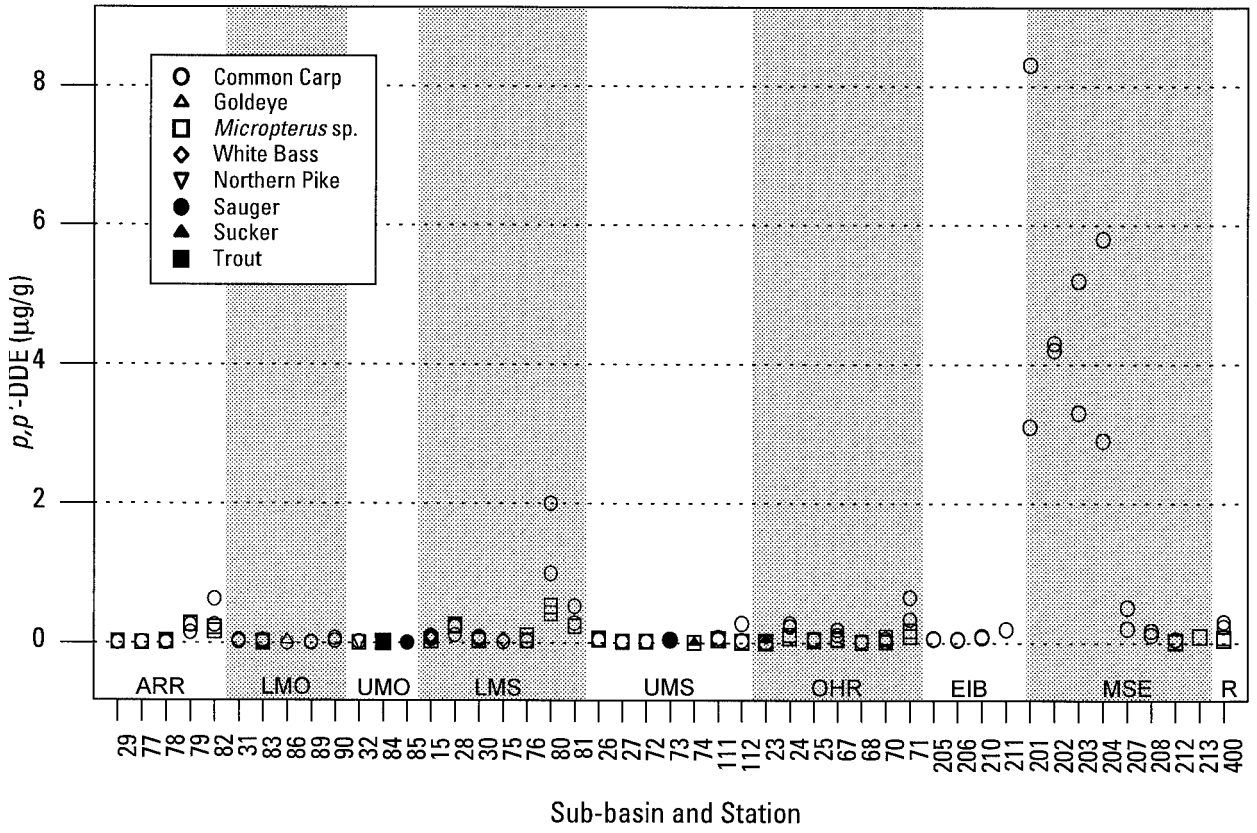

Fig. 2. Concentrations of *p,p′*-DDE in composite samples of whole fish, by station, subbasin, and taxon. Censored values are plotted as 0.005 µg/g (50% LOD). See Table 1 for station locations and subbasins

From 1970 to 1980-81, *p,p′*-DDE accounted for about 70% of total DDT (Schmitt *et al.* 1981, 1983, 1985), then increased to 73% in 1984 (Schmitt *et al.* 1990) and 74% in 1986 (Schmitt *et al.* 1999c), reflecting the reduced influx and continuing weathering of *p,p′*-DDT in the environment. In 1995, the average for MRB stations with detectable DDT residues was still about 75%. Residues of *p,p′*-DDE, were detected at all or nearly all NCBP stations in every collection from 1970 through 1986 (Schmitt *et al.* 1985, 1990, 1999c).

In terms of ecological risk, the U.S. Environmental Protection Agency (EPA) ambient water quality criterion for DDT (US EPA 1980) is based on a value of 0.15 µg/g (total DDT) in fish for the protection of reproduction in the brown pelican (*Pelicanus occidentalis*), the most sensitive species evaluated (Anderson *et al.* 1975); for other avian species, the range is 1–3 µg/g (Blus 1996). However, the Canadian wildlife value for total DDT is 0.14 µg/g (Environment Canada 1999) and the New York guideline is 0.2 µg/g (Newell *et al.* 1987). Relative to higher values of Blus (1996), the 1995 DDT residues in fish from NCBP and NAWQA sites in the lower MRB represent a hazard to most fish-eating birds (Figure 2). Using the lower values (US EPA 1980; Newell *et al.* 1987; Environment Canada 1999), sensitive species may also be at risk in the ARR and OHR subbasins and at the reference site. In laboratory-exposed freshwater fish, toxic effects have been observed at whole-body total DDT concentrations ≥ 0.5 µg/g in some studies (Jarvinen and Ankley 1999), but there is great variation among species and exposure regimes.

Toxaphene

Following the 1972 U.S. ban on DDT use, toxaphene became the insecticide most heavily used on cotton until it also was banned in the early 1980s (US EPA 1982). The geographic distribution of toxaphene residues among the 1995 samples reflects this historic use pattern. Toxaphene was detected in only 12 samples, all from five sites in the lower MRB—NCBP Station 80 (Yazoo R.) and NAWQA Stations 201–204, the latter all in the MSE Study Unit (data not shown). These represent only 7% of the samples and 11% of the stations (Table 2) and are the same sites at which total DDT concentrations were greatest (Figure 2). In 1986, toxaphene was detected at 64% of the NCBP stations at a twofold greater LOD (0.1 µg/g). The 1995 toxaphene concentrations at NCBP Station 80 were 0.8–2.5 µg/g in carp and 0.5–0.7 µg/g in largemouth bass (mean about 1 µg/g) but were generally higher (means 2.0–4.0 µg/g, maxima 2.0–>8.0 µg/g) in carp from Stations 201–204 (data not shown). Although elevated relative to other 1995 sites, levels at Station 80 declined substantially over the past two decades; concentrations were 0.4–2.4 µg/g in 1986 (Schmitt *et al.* 1999c) and 10–20 µg/g in the late 1970s

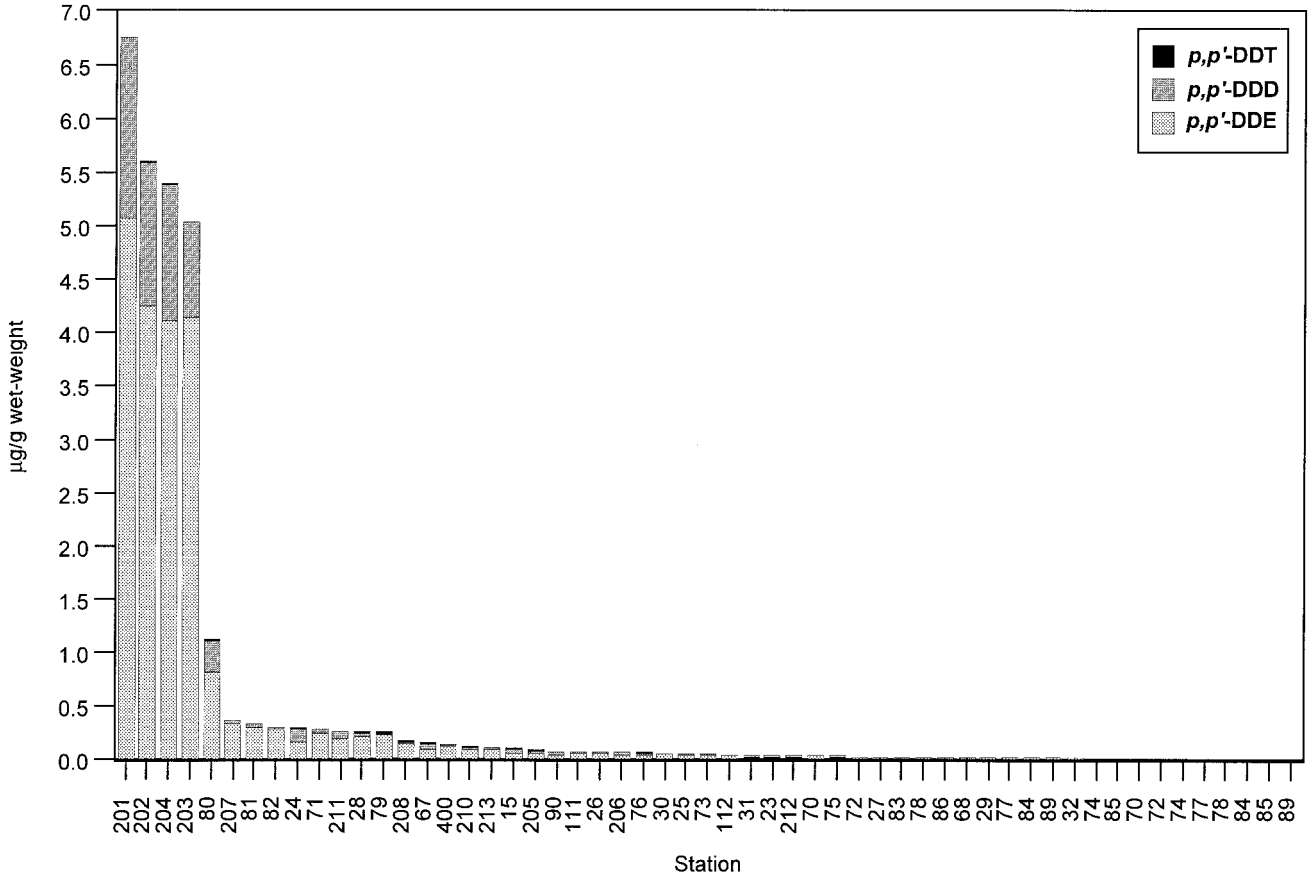

Fig. 3. Ranked geometric mean concentrations of *p,p′*-DDT homologs in composite samples of whole fish, by station. (Note: Censored values were represented by 50% of LOD in the totals and means but are not shown.) See Table 1 for station locations

and early 1980s (Schmitt *et al.* 1981,1983, 1985). Similar to the pattern observed for DDT, toxaphene concentrations in fish from NAWQA Stations 201–204 remained about at the levels observed at Station 80 in the early 1980s (Schmitt *et al.* 1983, 1985). In contrast to DDT, which declined by about 50% from 1986 to 1995, the geometric mean concentration of toxaphene at Station 80 was about the same in 1995 as in 1986; however, there were no taxa common to both collections at Station 80, so this comparison should be considered with caution. At NCBP stations with species common to both collections the trends were uniformly downward, however (data not shown).

Toxaphene is a complex mixture of chlorinated camphenes that is difficult to analyze by GC-ECD because of interferences from coeluting PCB congeners and other ubiquitous environmental residues. Consequently, negative chemical ionization (NCI) GC/MS is the preferred analytical method (Ribick *et al.* 1982; Muir and de Boer 1993). Nevertheless, reasonably good concentration estimates can be achieved by capillary-column GC-ECD if toxaphene is fractionated away from PCBs (*e.g.*, Krock *et al.* 1997), as was done with the 1995 samples; and concentrations of PCBs and chlordane are low relative to those of toxaphene, as was true in the 12 toxaphene-containing samples from stations in the MSE Study Unit and Station 80 (see following discussion). Nevertheless, the toxaphene concentrations reported here and in the past should be considered estimates.

Toxaphene is highly toxic to fish (Johnson and Finley 1980); adverse effects on freshwater fish have been associated with whole-body residues $\geq$ 1.0 µg/g in laboratory studies with technical toxaphene (Jarvinen and Ankley 1999), a level exceeded by some 1995 samples. However, all the samples from Station 80 and the MSE NAWQA sites exceeded 0.0063 µg/g, the Canadian wildlife guideline (Environment Canada 1999). Regardless, the composition and potential toxicity of differentially weathered toxaphene can vary greatly (Harder *et al.* 1983; Gooch and Matsumura 1987; Bidleman *et al.* 1993).

Cyclodiene Insecticides

The insecticides dieldrin; aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene), which is metabolized to dieldrin; chlordane (mixture of related compounds); and heptachlor (1,4,5,6,7,8,8-heptachloroepoxy-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene), which is metabolized to heptachlor epoxide, were used against a variety of soil-dwelling insects, including corn rootworms (*Diabrotica* spp.) and termites. These compounds bind tightly to soil particles and persist in many areas from historic uses (Schnoor 1981; Rostad 1997; Nowell *et al.* 1999). Endrin was used extensively on cotton and, to a lesser extent, against army

Table 3. Geometric mean concentrations of *p,p′*-DDE in composite samples of whole carp and bass, by subbasin and program (as defined in Table 1) and for the reference site in West Virginia (also shown are ANOVA F values, **p < 0.01)

	Taxon	
Subbasin or Program	Carp (F = 35.05**)	Bass (F = 18.82**)
Subbasins		
Arkansas-Red R.	0.11^{1}_{ac}	0.04_{a}
Lower Missouri R.	0.02_{b}	0.01_{b}
Upper Missouri R.	0.01_{b}	0.01_{b}
Lower Mississippi R.	0.15^{2}_{a}	0.12_{c}
Upper Mississippi R.	0.04_{c}	0.02_{bd}
Ohio R.	0.07^{3}_{ac}	0.04_{ad}
Eastern Iowa Basins	0.09_{c}	—[5]
Mississippi Embayment	1.00_{d}	0.04_{ad}
Reference	0.27_{a}	0.06_{ac}
Programs		
NCBP stations	0.05^{5}_{a}	0.03_{a}
NAWQA stations	0.29_{b}	0.04_{ab}
Reference	0.27_{b}	0.06_{b}

See text for statistical methods. Within each of the four groups, (taxa, subbasins, programs), means containing the same subscript are not significantly different (ANOVA, p > 0.05).
[1]Does not include Stations 29 or 77.
[2]Does not include Station 76.
[3]Does not include Station 23.
[4]Only carp were collected in the EIB study unit.
[5]Does not include Stations 23, 29, 76, or 77.

cutworms (*Euoxoa axilliaris*) infesting wheat in the Great Plains and to protect orchards from rodents (Schmitt *et al.* 1990). Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide) is the only cyclodiene pesticide currently used in North America, but others are synthesized domestically for export.

Dieldrin: Greatest concentrations of dieldrin were historically found in fish from the Midwest (see Schmitt *et al.* [1999c] and references therein). In the MRB, this pattern persisted into 1995; dieldrin residues were present in 42% of the samples from 57% of the stations, at concentrations ranging from barely detectable (about 0.01 μg/g) to 0.25 μg/g (Figure 4, Table 2). Greatest 1995 concentrations occurred in the central and southern parts of the basin, as they have historically. Geometric station means were > 0.025 μg/g at NCBP Stations 76 (Mississippi R. at Memphis, TN), 26 (Illinois R. at Hardin, IL), 68 (Wabash R. at New Harmony, IN), 73 (Des Moines R. at Keosauqua, IA), 75 (Mississippi R. at Cape Girardeau, MO), 31 (White R. at Devall's Bluff, AR), 83 (Missouri R. at Hermann, MO), 80 (Yazoo R.), and 90 (Kansas R. at Bonner Springs, KS) and at NAWQA Stations 205, 206 and 210, in the EIB Study Unit (data not shown). The greatest individual sample concentrations (0.10–0.25 μg/g) were from Stations 76, 206, 83, 68, and 67 (Allegheny R. at Natrona, PA; Figure 4, Table 2). Concentrations at most sites in the central MRB compare favorably to 1992–93 values reported for the South Platte River system by Tate and Heiny (1996) and confirm the presence of relatively high values in fish from agricultural and urban watersheds in Iowa (Roberts 1997); however, the 1995 MRB maxima were at least twice those reported by either of the latter studies. No dieldrin residues were detected in samples from the reference site (Figure 4).

From the mid-1980s to 1995, dieldrin concentrations declined by 50% or more at most of the NCBP stations in the MRB with the greatest historic concentrations (*c.f.* Schmitt *et al.* 1990, 1999c). This finding supports other research showing that significant amounts of this and other soil-associated compounds were transported out of the MRB by the floods of 1993 and 1995 (Rostad 1997). Dieldrin concentrations were also relatively high in the past at NCBP Station 90 (Kansas R.), which was not sampled in 1986; however, compared to 1984, concentrations there also declined but not to the extent that it did at other stations. Station 76 was an exception in that concentrations were twice as high in 1995 than in 1986. Some of this increase may reflect taxonomic differences; freshwater drum (*Aplodinotus grunniens*) and bluegill were collected in 1986, whereas carp and largemouth bass were collected in 1995. Carp were collected in 1984, however, when concentrations were 0.08–0.11 μg/g (Schmitt *et al.* 1990)—about 50% lower than in 1995 (Figure 4). Although some of the elevated cyclodiene pesticide levels in fish from Station 76 can no doubt be attributed to agricultural pesticide use in the Midwest and termite control efforts in Memphis and elsewhere in the MRB (Nowell *et al.* 1999), high concentration of dieldrin, endrin, and other cyclodiene insecticides at this site have long been attributed to a manufacturing source near Memphis (Schmitt *et al.* 1981, 1983, 1985, 1990, 1999c) and from a landfill containing pesticide manufacturing wastes (Leppanen *et al.* 1998). In the past, chemical spills at the manufacturing site caused massive fish kills (Biglane *et al.* 1964), and fish from the Mississippi River contained residues of cyclodiene insecticide precursors (Yurawecz and Roach 1978). Among other NCBP stations with taxa in common to the 1986 and 1995 collections, dieldrin concentrations declined or changed only slightly at most (data not shown). The exception was Stations 67 (Allegheny R.), where concentrations in carp also increased.

Adverse effects have been observed in laboratory studies with freshwater fish at whole-body dieldrin concentrations ≥ 1.2–1.4 μg/g (Jarvinen and Ankley 1999), which is about fivefold greater than the highest 1995 concentration (about 0.25 μg/g at Station 76; Figure 4). This concentration is also more than 10-fold lower than dietary concentrations associated with adverse effects in wildlife (see review by Peakall [1996]). However, it is only twice the NYSDEC wildlife guideline of 0.12 μg/g (Newell *et al.* 1987). Based on this lower value, dieldrin residues in fish from Station 206 may also represent a hazard to piscivorous wildlife (Figure 4). Evidence cited by Schmitt *et al.* (1985, 1990) suggested that dieldrin was still being carried into receiving waters from fields in the Midwest, despite the fact that no aldrin (the source of most environmental dieldrin residues) had been used in agriculture since 1974 (Schnoor 1981). The more recent data of Rostad (1997) and the 50% lower concentrations present in fish in 1995 relative to 1986 indicate that these compounds are still present, but concentrations are generally low and declining.

Endrin: Low concentrations of endrin (about 0.2 μg/g) were historically present in fish from NCBP sites in the South and Midwest (Schmitt *et al.* 1981, 1983, 1985, 1990, 1999c). Al-

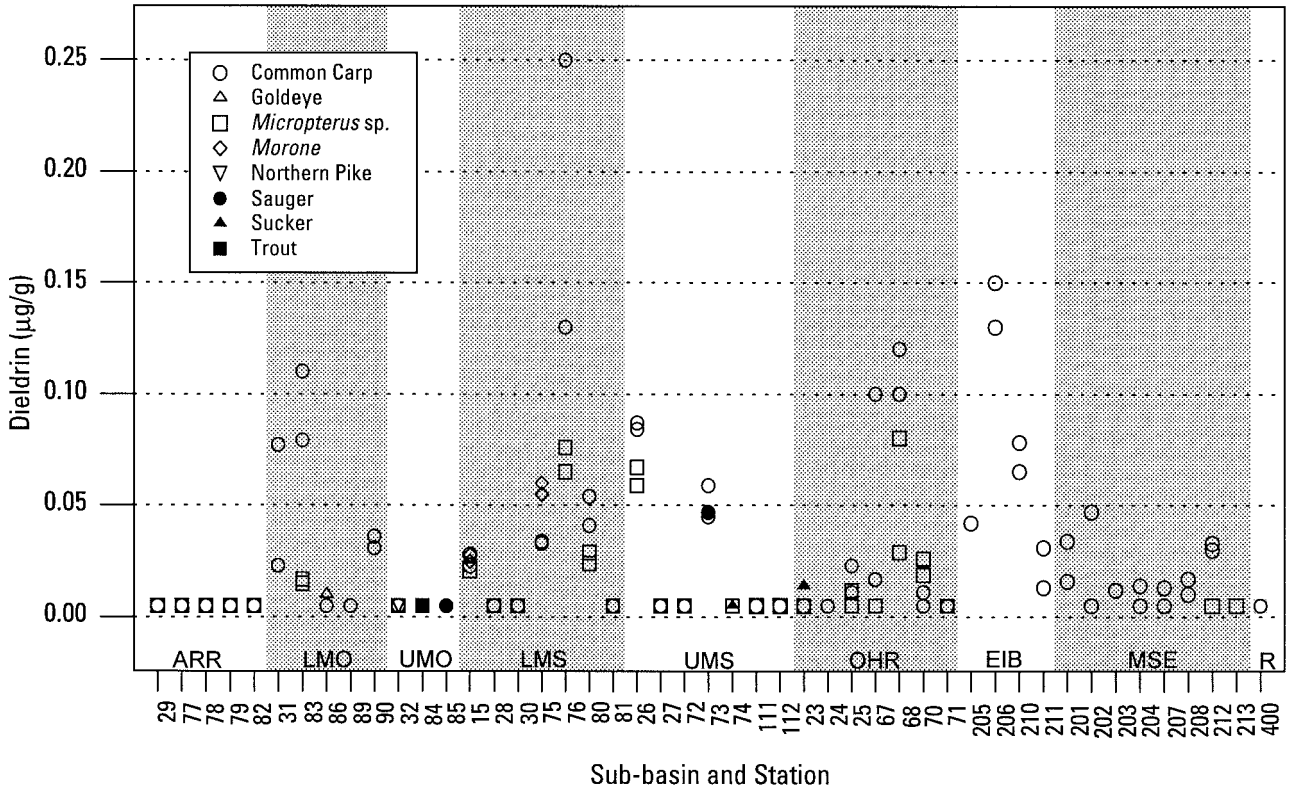

Fig. 4. Concentrations of dieldrin in composite samples of whole fish, by station, subbasin, and taxon. Censored values are plotted as 0.005 µg/g (50% LOD). See Table 1 for station locations and subbasins

though banned for most uses in 1984, it was used sporadically in the northern Great Plains through the 1980s, and Tate and Heiny (1996) detected 0.1–0.2 µg/g of endrin in fish collected from the Platte River system in 1992–93. In 1995, endrin was present in only four samples (Table 2), all from NCBP Station 76 (Mississippi R. at Memphis). This site historically produced the highest endrin concentrations among NCBP stations (Schmitt *et al.* 1999c) owing to the point sources described previously. The 1995 concentrations at Station 76 were 0.22 µg/g in largemouth bass (both samples) and 0.40–0.71 µg/g in carp (geometric station mean 0.34 µg/g; data not shown), which is about fivefold greater than the 1986 mean for bluegill and freshwater drum from that site. In 1984, the concentrations in carp were 0.01–0.22 µg/g (Schmitt *et al.* 1990).

Endrin is among the most toxic organochlorine insecticides to fish (Grant 1976; Johnson and Finley 1980). In laboratory studies with freshwater fish, adverse effects have been observed at whole-body concentrations as low as 0.01 µg/g (Jarvinen and Ankley 1999), the nominal 1995 detection limit exceeded only by the samples from Station 76. In contrast to the safety margin observed for dieldrin, the 1995 endrin concentrations (0.2–0.7 µg/g) in Station 76 carp from were only about two- to fourfold lower than the lowest dietary concentrations known to be toxic to avian wildlife (see review by Peakall [1996]). Station 76 concentrations were 10-fold greater than the New York wildlife guideline (Newell *et al.* 1987), however.

Chlordane and Heptachlor: Residues of chlordane components, heptachlor (as heptachlor epoxide), and their metabolites were among the most widely distributed organochlorine compounds detected in the 1995 samples. Residues of at least one of the measured chlordane-related compounds (*cis*-chordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, and heptachlor epoxide) were present in 51% of the samples from 70% of the stations sampled (Table 2). None were detected in any of the samples from Station 400 (reference site). The geographic distribution of these compounds closely resembled that of dieldrin. The greatest mean total concentrations (0.07–0.25 µg/g) of chlordane-related compounds occurred in the central and southern parts of the MRB—at NCBP Stations 76 (Mississippi R. at Memphis), 68 (Wabash R. at New Harmony, IN), 23 (Kanawha R. at Nitro, WV), 24 (Ohio R. at Marietta, OH), 67 (Allegheny R. at Natrona, PA), 73 (Des Moines R. at Keosauqa, IA), 90 (Kansas R. at Bonner Springs, KS), and 26 (Illinois R. at Hardin, IL) and at NAWQA Stations 206 (Iowa R. at Morengo R., IA), 205 (S. Skunk R. at Oskaloosa, IA), and 201 (Big Sunflower R. at Anguilla, MS; Figure 5 and 6). The individual samples containing the highest concentrations (0.25–0.55 µg/g of total chlordane-related compounds) were the two carp samples from Station 76, one carp sample from Station 206, and one each of bass and smallmouth buffalo from Station 23 (Figure 5, Table 2). These concentrations are about fivefold greater than the maximum 1992–93 concentrations reported for urban and mixed land-use sites in the Platte River system by Tate and Heiny (1996), but they

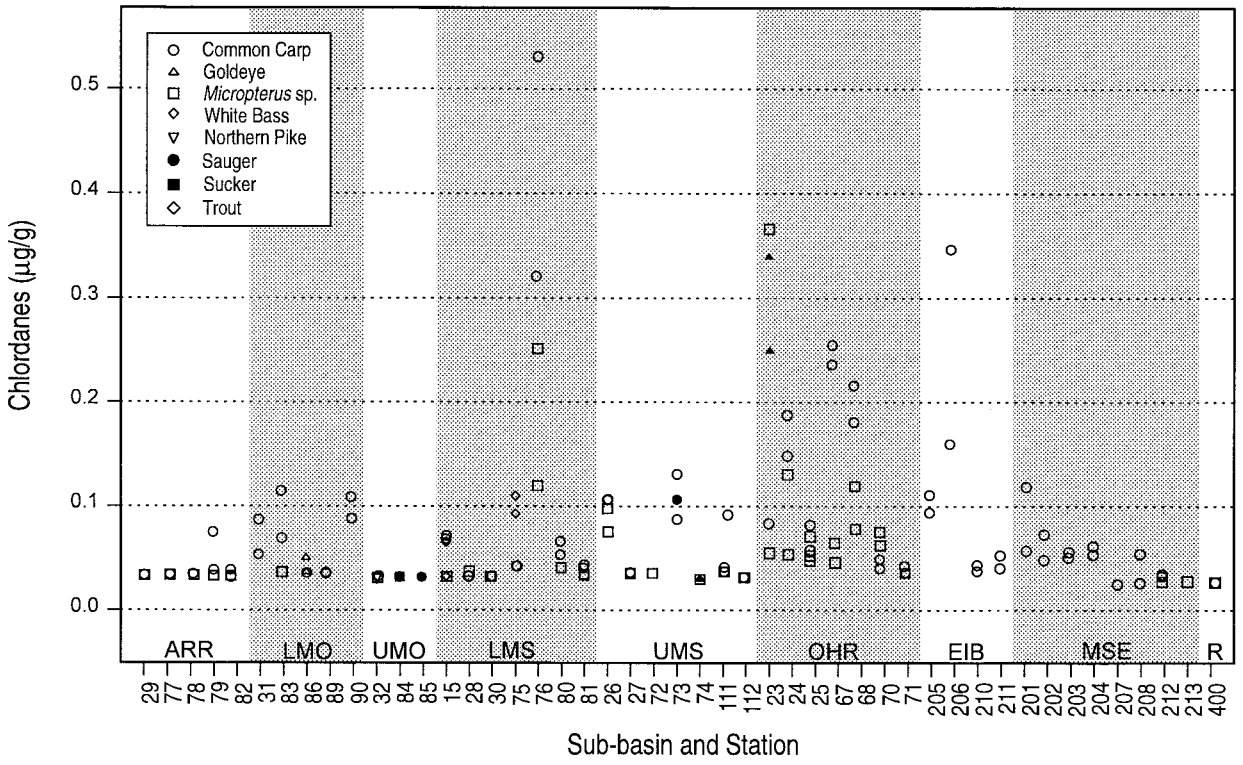

Fig. 5. Concentrations of total chlordane-related residues (sum of *cis*- and *trans*-chlordanes and nonachlors; oxychlordane; and heptachlor epoxide) in composite samples of whole fish, by station, subbasin, and taxon. Censored values were represented as 0.005 µg/g (50% LOD) for each compound. See Table 1 for station locations and subbasins

compare favorably with those reported for agricultural areas of Iowa by Roberts (1997). In 1984, the most recent NCBP collection in which carp were collected from Station 23, concentrations at that site were about the same as in 1995—0.21–0.59 µg/g (Schmitt *et al.* 1999c).

Heptachlor, aldrin, dieldrin, and chlordane were all used against ants, termites, corn rootworms, and other soil-dwelling insects, and residues of the individual compounds and their metabolites therefore tend to co-occur (Schmitt *et al.* 1990). Heptachlor also occurs as a minor component ($\leq$ 10%) of technical chlordane (NRCC 1974), and small amounts of *cis*- and *trans*-chlordane are present in technical heptachlor (Eisler 1990; Wiemeyer 1996). It is therefore difficult to differentiate the source(s) of environmental heptachlor- and chlordane-derived residues (Schmitt *et al.* 1985). Heptachlor is rapidly converted to heptachlor epoxide and other metabolites by many organisms, and the use of this compound was phased out by the early 1980s (Wiemeyer 1996). Consequently, little or no unmetabolized heptachlor was detected in NCBP fish samples after 1976–77. Both the occurrence and the concentrations of heptachlor epoxide were declining through the mid-1980s; in 1986, concentrations were $\geq$ 0.04 µg/g in one or more samples from only NCBP Stations 75 (Mississippi R. at Cape Girardeau, MO), 26 (Illinois R. at Hardin, IL), and 83 (Missouri R. at Hermann, MO) (Schmitt *et al.* 1999c). In 1995, residues of heptachlor epoxide were present in only 14 samples (9%) from seven stations (15%), mostly as trace concentrations ($<$ 0.02 µg/g). Greater-than-trace concentrations (0.03–0.05 µg/g) were present only in carp from NAWQA Station 206 (Iowa R. at Morengo, IA; Table 2, Figure 6).

The 1995 concentrations of chlordane-related compounds were lower at most NCBP sites than they were in 1986 (Schmitt *et al.* 1999c). Nationally, chlordane concentrations declined steadily from 1976 to 1981 (Schmitt *et al.* 1983, 1985), but then changed little from 1980–81 to 1986 (Schmitt *et al.* 1990, 1999c). As described for other cyclodiene insecticides, Station 76 was an exception; concentrations were higher in 1995 than in 1986, with the same caveat that different taxa were collected in 1995. Chlordane concentrations generally declined or changed little at stations with taxa in common to both collections (data not shown).

The incidence of the most abundant and persistent chlordane constituents has been declining since the early 1980s. In 1980–81, *cis*-chlordane was detected at 74% of the NCBP stations sampled and *trans*-nonachlor at 85%, having declined from 93% in 1978–79 (Schmitt *et al.* 1983, 1985). By 1984–86, residues of *cis*-chlordane and *trans*-nonachlor were present at only 70% and 74%, respectively, of the NCBP stations sampled (Schmitt *et al.* 1990, 1999c). In 1995, *trans*-nonachlor was again the most frequently detected chlordane constituent; it was present 51% of the samples from 70% of the stations (Table 2). Residues of *cis*-chlordane were next in concentration and abundance (21% of the samples from 48% of the stations; Table 2). At Stations 76, however, *trans*-chlordane was the most abundant component in 1995 (Figure 6), which may reflect the influence of the point sources noted for dieldrin and endrin. In

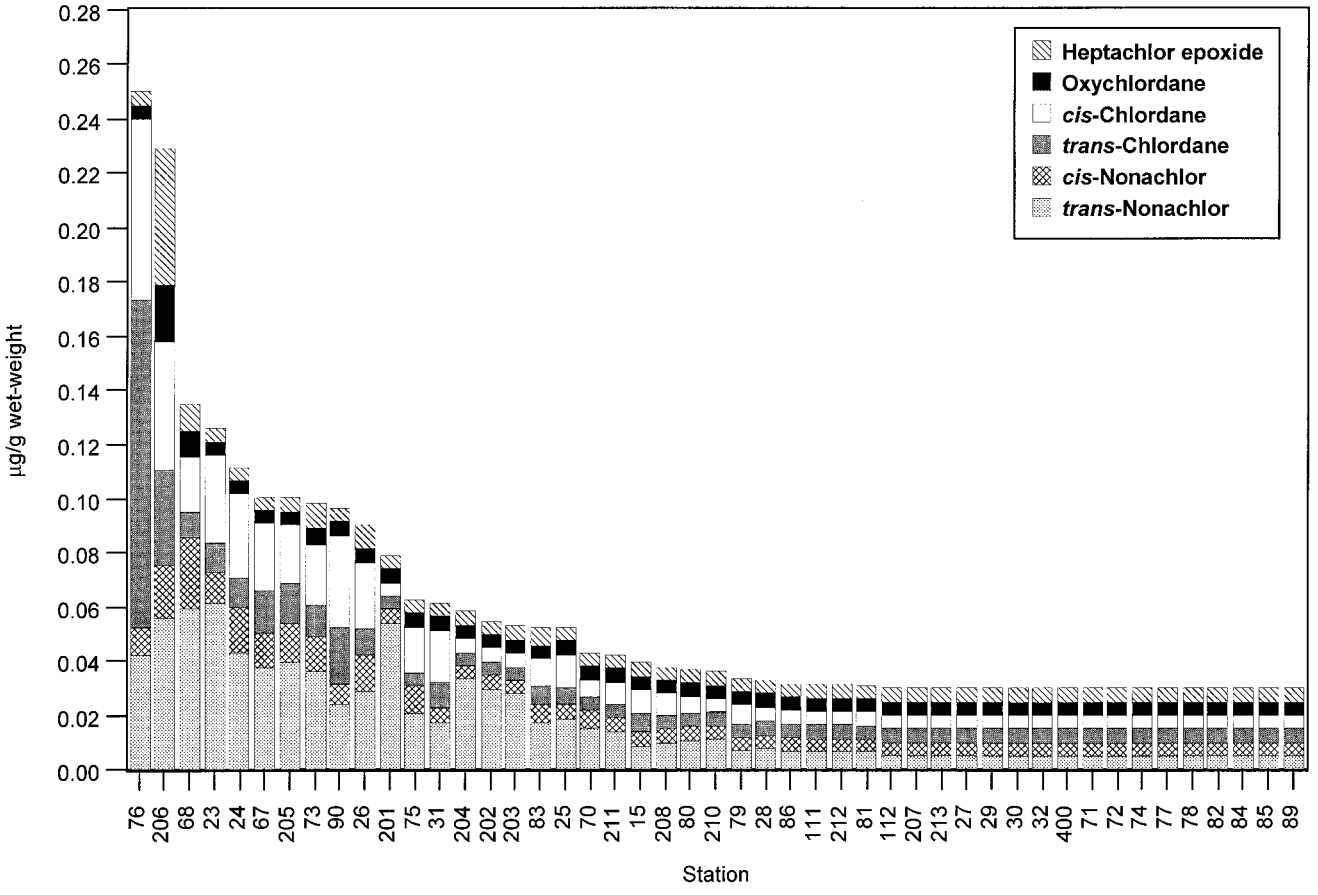

Fig. 6. Ranked geometric mean concentrations of chlordane-related compounds in composite samples of whole fish, by station. (Note: Censored values were represented by 50% of LOD in the totals and means but are not shown.) See Table 1 for station locations

1986, the maximum chlordane concentration (0.78 µg/g) occurred at NCBP Station 69 (Ohio R. at Cincinnati, OH), which was not sampled in 1995, and relatively high concentrations of one or more chlordane-related compounds (*cis*- or *trans*-chlordane or nonachlor; oxychlordane; heptachlor epoxide) were also present in fish from Stations 70 (Ohio R. at Metropolis, IL), 83 (Missouri R. at Hermann, MO), and 67 (Allegheny R.).

Oxychlordane, a highly toxic metabolite of *cis*-chlordane, and heptachlor epoxide were also present at most of these sites in 1986 but at lower concentrations than the other chlordane components. As noted for dieldrin, chlordane concentrations were also relatively high in the past at NCBP Station 90 (Kansas R.), which was not sampled in 1986. In 1995 chlordane concentrations at Station 90 were about the same as they were in 1984 (geometric mean 0.03 µg/g). In general, the compositional change in the chlordane mixture present in fish collected in 1995 compared to 1986 reflects the continued weathering of these compounds, and the decline in concentrations at most NCBP sites from 1986 to 1995 further supports the hypothesis that large quantities of cyclodiene insecticides were transported out of the MRB by the floods of 1993 and 1995 (Rostad 1997).

In terms of ecological risk, a total concentration of 0.3 µg/g for *cis*-chlordane, *trans*-chlordane, and oxychlordane in whole fish was proposed as a temporary guideline for vertebrate wildlife protection (Eisler 1990). This level was exceeded by some of the most heavily contaminated 1995 samples (Table 2, Figure 5), but not by any geometric station means (Figure 6). Only one sample from Station 76 exceeded 0.5 µg/g, the New York wildlife guideline for chlordanes (Newell *et al.* 1987). In laboratory exposures of freshwater fish, the lowest heptachlor and heptachlor epoxide residue concentrations associated with adverse effects are several orders of magnitude greater than levels present in the 1995 samples (Jarvinen and Ankley 1999), but there are no data for chlordane. Paddlefish (*Polyodon spathula*) eggs from the Ohio River collected in 1997 contained 0.35 µg/g of chlordane and 0.74 µg/g of PCBs (Gundersen *et al.* 2000), similar to levels observed in the 1995 samples from the OHR subbasin (Figure 6). The testes of male Ohio River paddlefish contained fourfold greater concentrations and possible contaminant-related effects on the adult fish, but not on hatching success, were noted (Gundersen *et al.* 2000).

Hexachlorocyclohexane (HCH)

HCH (also known as benzene hexachloride, BHC) is a mixture of five 1,2,3,4,5,6-hexachlorocyclohexane isomers that was formerly used extensively on cotton and other crops. Technical HCH use in the United States was curtailed in the late 1970s, but it remained in use elsewhere into the

1990s (Li et al. 1996). The purified γ-isomer (lindane), which also contains small amounts of the other isomers, is still used in North America for a few agricultural and domestic applications (Li *et al.* 1996; Poissant and Koprivnjak 1996). The 1995 samples were analyzed for four HCH isomers (α, β, γ, and δ), but no residues were detected (Table 2). HCH isomers are comparatively volatile and rapidly cleared by fish (Butte *et al.* 1991; Willett *et al.* 1998). Residues occurred infrequently and at low concentrations in NCBP fish samples, and both incidence and concentrations of the two isomers measured historically (α and γ) were declining through the mid-1980s (Schmitt *et al.* 1999c).

Mirex

Mirex is a highly recalcitrant compound used historically as a fire retardant and as an insecticide to control red imported fire ants (*Solenopsis invicta*) in the South (Kaiser 1987). The historic distribution of mirex in NCBP samples reflected these patterns: residues greater than trace concentrations were found only at sites in the South, from insecticidal use; and in the Great Lakes basin, from point-source discharges (Kaiser 1987; Schmitt *et al.* 1990, 1999c). Concentrations in fish from both areas had been declining through 1986 (Schmitt *et al.* 1999c). In 1995, mirex was detected (≥ 0.01 μg/g) in only four samples (4%) from two sites (4%, Table 2) in Louisiana—NCBP Station 81 (Red R. at Alexandria) and NAWQA Station 204 (Tensas R. at Tenda), the latter in the MSE Study Unit (data not shown). In 1986, traces of mirex were also present in fish from NCBP Stations 25 (Tennessee R. at Clarksville, TN) and 69 (Ohio R. at Cincinnati) at concentrations of 0.02–0.075 μg/g. Concentrations at Station 81 were 0.02–0.04 μg/g in 1995, slightly higher than they were in 1986 (0.01–0.02 μg/g); however, different species were collected in 1995 (carp and largemouth bass) than in 1986 (channel catfish and white bass). At stations with taxa common to both the 1986 and 1995 collections, mirex concentrations changed little (data not shown). Eisler (1985) stated that sensitive wildlife species are affected at dietary mirex levels of 0.1 μg/g, a level that was approached but not exceeded by any sample collected in 1995 (Table 2). In laboratory-exposed freshwater fish, toxic effects have been observed at concentrations ≥ 0.35 μg/g (Jarvinen and Ankley 1999), and the NYSDEC wildlife guideline is 0.33 μg/g (Newell *et al.* 1987), both of which are about eightfold greater than the highest 1995 concentrations.

Hexachlorobenzene (HCB)

Hexachlorobenzene (HCB) is virtually ubiquitous (Zell and Ballschmiter 1980). Environmental residues occur from the use of HCB a fungicide (Vizethum and Goerz 1979) and because HCB is a by-product of the production of other chlorinated hydrocarbons (Villanueva *et al.* 1974). HCB is shorter-lived (Villanueva *et al.* 1974) and much less toxic (Jarvinen and Ankley 1999) than DDT and most other persistent organochlorine compounds; however, commercial formulations once contained toxic impurities, including polychlorinated dibenzo-*p*-dioxins and -dibenzofurans (Villanueva *et al.* 1974). In addition, HCB has a low level of dioxin-like activity (about 0.0001–0.001 relative to 2,3,7,8-TCDD—Hahn *et al.* 1996; Sinclair *et al.* 1997), and may therefore contribute to toxicity in combination with other polyhalogenated hydrocarbons. In 1995, HCB residues were detected (about 0.01 μg/g) in only four samples (2%) from three sites (7%, Table 2): NCBP Stations 24 (Ohio R. at Marietta, OH), 76 (Mississippi R. at Memphis), and 23 (Kanawha R. at Nitro, WV). Concentrations in these samples were 0.020–0.075 μg/g (data not shown), which are at least 10-fold lower than Canadian wildlife guidelines (Environment Canada 1999). In 1986, traces (< 0.02 μg/g) of HCB were also present in fish from NCBP Stations 15 (Mississippi R. at Luling, LA), 81 (Red R. at Alexandria, LA) and 69 (Ohio R. at Cincinnati, which was not sampled in 1995) but not at the three sites where was detected in 1995.

PCBs

PCBs were used in a wide variety of commercial and industrial applications (Hutzinger *et al.* 1974). In 1995, residues in fish continued a downward trend in concentration and occurrence evident since the early 1980s; PCBs were detected (≥ 0.05 μg/g) in only 21% of the samples from 35% of the stations (Table 2), and none were detected in any samples from the reference site (Figure 7). In 1986 PCBs were detected at 65% of the NCBP stations nationwide and at 25 of the 34 NCBP stations (73%) sampled in 1995 (Schmitt *et al.* 1999c). PCBs were also detected in 1984 at Station 90, which was not sampled in 1986 (Schmitt *et al.* 1990). In 1986, PCBs were not detected in any samples from Stations 30 (White R.), 32 (Missouri R. at Garrison Dam), 74 (Mississippi R. at Little Falls, MN), 77 (Arkansas R. at John Martin Res.), 78 (Verdigris R.), 84 (Big Horn R.), 85 (Yellowstone R.), 86 (James R.), or 88 (S. Platte R. at L. McConaughy, NE, which was not sampled in 1995), nor were any detected at most of these stations in 1995; traces were present in samples from Stations 30 and 86, however. From 1976–84, PCBs were present at about 91% of the NCBP stations nationwide (Schmitt *et al.* 1990). It should be noted that the declining incidence of PCBs in the MRB from 1984–86 to 1995 occurred despite the lower LOD for total PCBs in 1995 (0.05 μg/g) than in 1984–86 (0.1 μg/g); however, GC-ECD-based analyses of weathered PCBs based on Aroclor mixtures can vary considerably (Schwartz *et al.* 1987; Eganhouse and Gossett 1991), and the quantitation method used for the 1995 samples differed slightly from that used in 1984–86 (Schmitt *et al.* 1990).

Within the MRB, greatest 1995 PCB concentrations occurred at stations in the OHR and UMS subbasins, as they did in the past, and lowest levels were in the EIB and MSE Study Units (Figure 7). The values in carp from the EIB sites (≤ 0.12 μg/g) were slightly lower than those reported by Roberts (1997) for some EIB carp and by Tate and Heiny (1996) for carp from some sites in the Platte River system, differences possibly attributable to differing analytical methods. Concentrations of 1.0–3.2 μg/g in individual 1995 samples and station means > 0.3 μg/g occurred at NCBP Stations 24 (Ohio R. at Marietta, OH), 23 (Kanawha R. at Nitro, WV), 67 (Allegheny R.), 76 (Mississippi R. at Memphis), 111 (Mis-

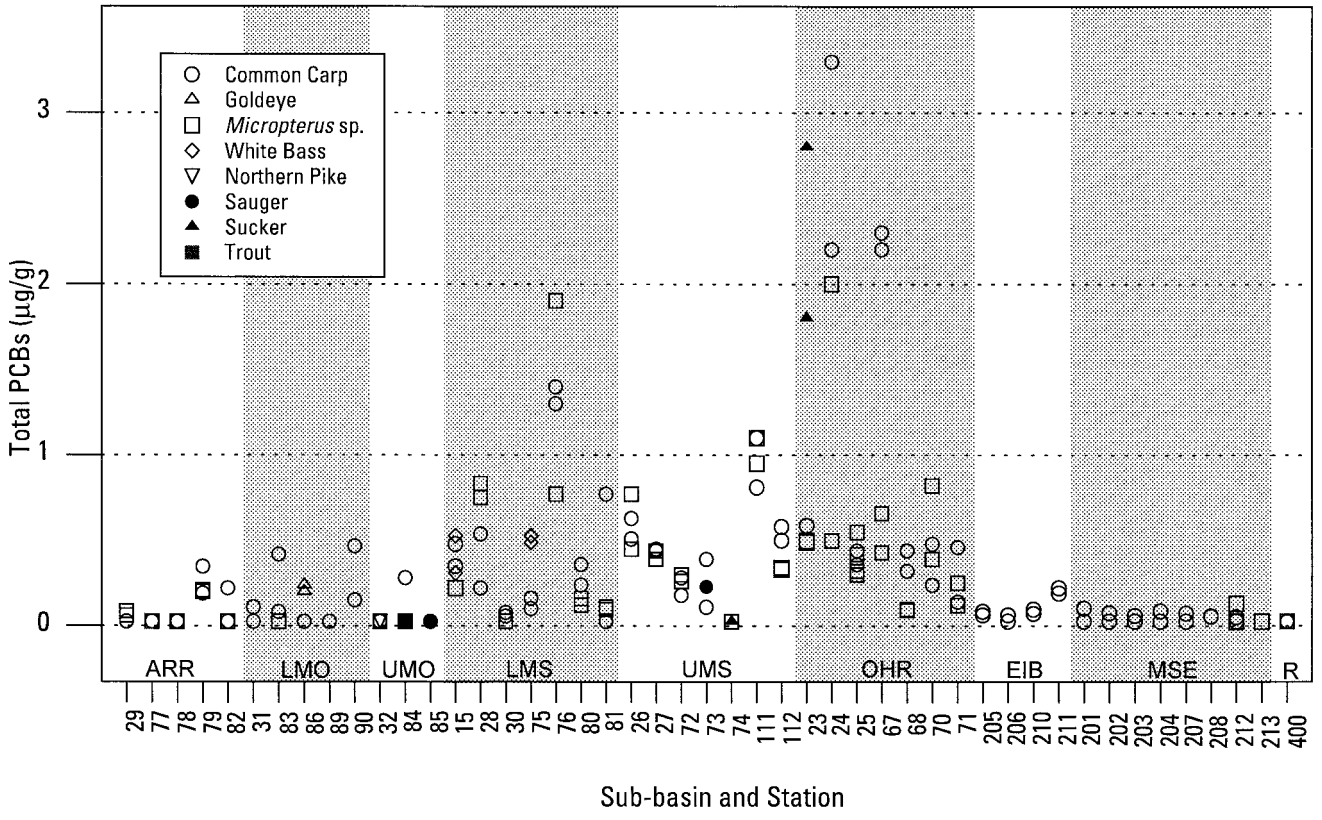

Fig. 7. Concentrations of total PCBs in composite samples of whole fish, by station, subbasin, and taxon. Censored values are plotted as 0.025 µg/g (50% LOD). See Table 1 for station locations and subbasins

sissippi R. at Lake City, MN), 26 (Illinois R.), 28 (Arkansas R.), 70 (Ohio R. at Metropolis, IL), 27 (Mississippi R. at Guttenburg, IA), 112 (Mississippi R. at Dubuque, IA), 25 (Cumberland R. at Clarksville, TN), and 15 (Mississippi R. at Luling, LA; Figure 7). At most of these sites, mean concentrations either declined substantially (Stations 23, 81, 111, and 24) or did not change appreciably since the mid-1980s (Schmitt *et al.* 1999c; Zajicek *et al.* 2000; data not shown). Lee and Anderson (1998) also reported declining PCB concentrations in carp and walleye from urbanized areas of the MRB in Minnesota during 1975–95. Total PCB concentrations increased slightly at Stations 112, 28, and 76, however. Although there was a change in the species collected at some of these sites from 1986 to 1995 (especially at Station 28, where channel catfish and white crappie were replace by carp and largemouth bass; and at Station 76, as already noted), at the other sites at least one species was common to both collections. In within-taxon comparisons, total PCB concentrations in carp increased at Stations 75 (Mississippi R. at Cape Girardeau, MO), 70 (Ohio R. at Metropolis, IL), 111 (Mississippi R. at Lake City, MN), and 67 (Allegheny R.; data not shown). Concentrations declined in carp at Station 112 (Mississippi R. at Dubuque, IA) and in spotted bass at Station 25 (Cumberland R. at Clarksville, TN).

The New York wildlife guideline for total PCBs in fish is 0.11 µg/g (Newell *et al.* 1987), a concentration exceeded by at least one sample from Stations 76, 23, 24, and 67 (Figure 7). However, the toxicity of individual PCB congeners ranges over several orders of magnitude (Ahlborg *et al.* 1994; van den Berg *et al.* 1998) and varies with the endpoint being considered (Hansen 1998). The congener composition of weathered PCBs also varies greatly among NCBP locations and taxa (Zajicek *et al.* 2000). Toxicity of PCB congeners and other dioxin-like compounds occurs through multiple mechanisms, both aryl hydrocarbon hydroxylase (AhR) and non-AhR-mediated. In addition, there are profound differences among taxa with respect to the uptake and metabolism of PCB congeners. Carp (especially) accumulate lower-chlorinated congeners that may exhibit thyroid-, neuro-, or endocrine-mediated toxicity (Gerstenberger *et al.* 1997). Therefore, the ecological risk represented by PCB residues in the 1995 fish samples is unknown.

Summary and Conclusions

With few exceptions, organochlorine chemical residues were detected at fewer stations and at lower concentrations in 1995 than at any time since monitoring began in the mid-1960s. Residues derived from DDT (primarily as *p,p′*-DDE) were detected at all stations sampled (including the reference site), but potentially toxic (to fish-eating wildlife) concentrations ($>$ 1.0 µg/g) were found only in the MSE NAWQA Study Unit, where the greatest concentrations occurred; and in the Yazoo River in Mississippi, where concentrations were elevated historically. These sites are all in the Lower Mississippi

valley and drain watersheds farmed extensively for cotton. However, even at these sites little or no *p,p′*-DDT was detected, indicating the continued weathering of residual DDT rather than the input of new material. Concentrations of DDT were also low at NCBP stations on the Arkansans and Tennessee Rivers that were historically influenced by point sources of contamination. Disproportionately high concentrations of *o,p′*-DDT homologs and traces of *p,p′*-DDT in fish from one site (Ohio R. at Marietta, OH) suggests more recent inputs, however. Toxaphene was also present only at sites in the Lower Mississippi valley. Because of the historically heavy use of DDT and toxaphene on cotton, average concentrations were greatest in the LMS subbasin and MSE Study Unit. Traces of mirex, which was used primarily in the South against red imported fire ants, were detected at only two sites in Louisiana.

Cyclodiene pesticide residues were detected at fewer stations (70%) than DDT, but relatively high concentrations were more widespread. Although lower than levels reported in the past, relatively high concentrations of one or more cyclodiene residues (dieldrin, endrin, and chlordane-heptachlor) were present at sites in all subbasins except the ARR and UMO. Concentrations were generally highest in the EIB Study Unit and at most of the NCBP sites draining the cotton- and corn-producing regions of the central MRB, which encompasses parts of the UMS, LMS, OHR, and LMO subbasins. Cyclodiene pesticide concentrations were especially high in fish from the Mississippi River at Memphis, TN, where there are several point sources and where levels have been high in the past. Concentrations of all other organochlorine pesticides were very low.

PCB residues were detected at only 35% of the stations sampled and concentrations were generally low. Levels > 1.0 μg/g occurred only in fish from three sites in the OHR subbasin and from one each in the UMS and LMS subbasins, where mean concentrations were also greatest. PCB concentrations were generally lowest in the NAWQA Study Units (EIB and MSE), which drain primarily agricultural areas, and greatest at the NCBP stations near industrial and urban areas. Traces of HCB were detected at only two sites in the industrialized OHR sub-basin and in the Mississippi River at Memphis, TN.

The 1995 results confirm the continued weathering and redistribution of many organochlorine chemicals. Results from the MSE and EIB Study Units nevertheless indicate that considerable amounts of persistent pesticides remain in intensively farmed parts of the MRB and near point sources, from which they are available for transport and remobilization in aquatic ecosystems and where they may represent a continuing threat to terrestrial wildlife.

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