AN ANALYSIS OF FISH AND SEDIMENT SAMPLES FROM MISSISSIPPI DELTA RIVERS

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INTRODUCTION

The results presented in this paper were developed as part of the USDA Natural Resources Conservation Service's (NRCS) Delta Water Supply Study. The study was initiated by request to NRCS from the YMD Joint Water Management District and Delta Soil and Water Conservation Districts to determine the feasibility of stabilizing groundwater levels in the Mississippi River Alluvial Aquifer (aquifer). The issues of water supply and water quality in the Mississippi Delta are locked together by many relationships including aquifer level influence on baseflows in internal streams. Adequate baseflows are essential to a healthy stream environment.

The Mississippi Delta is home to many people who rely on subsistence fishing in local streams and rivers. For this reason, it is important to determine if this food supply is safe to eat. NRCS began testing water quality samples in the Delta in 1993 (Pennington 1996). There are now 22 water sampling locations (Figure 1) on the major internal Delta rivers. We collected catfish and stream bed sediment samples for pesticide and metal testing during May to August 1995. Sampling for fish and sediments included two locations each on Deer Creek (2 and 6), Bogue Phalia (15 and 16), Sunflower River (14 and 13) and Quiver River (17 and 18), and one at Yazoo Pass (10), Coldwater River (11) and Mill Creek (12). Testing has been completed on 41 catfish samples and 11 stream bed sediment samples representing the major internal Delta waterways.

Fish sampling was limited to catfish because: a) we felt that with our sampling technique, catfish would be found at each site allowing site comparisons, and b) catfish are a favorite food choice. Species collected included yellow bullhead catfish (*Ameriurus natalis*), channel catfish (*Ictalurus punctatis*), blue catfish (*Ictalurus furcatus*), and flathead catfish (*Pylodictus olivaris*). Nineteen samples were tested as fillet portions to determine the concentration of pesticides in the edible portion of the fish. Twenty two samples were tested as whole fish to be able to compare results to historic data.

Sediment samples were collected at each site to characterize pesticides and metals in the habitat of benthic dwellers, a major catfish food supply.

METHODOLOGIES

Catfish were collected using trotlines. Sampling required a minimum of two days per site. Lines were baited with shad, placed in the water, and checked the next day. Repeat sampling was done if the catfish were not caught. All catfish were placed on ice, taken to the field office, labeled, wrapped in foil, and frozen on the day they were caught. Frozen samples were delivered to Mississippi State Chemical Laboratory (MSCL) for testing.

Samples for pesticide analysis were defrosted and either filleted or left as whole fish. Samples were ground for analysis. Extraction, concentration, testing and quantification were done using techniques developed by the US Department of the Interior, Fish and Wildlife Service, Patuxent Wildlife Research Center in Laurel, Maryland, (Patuxent 1994) or listed in the US Department of Health and Human Services, Food and Drug Administration (FDA) manual on pesticide testing (McMahon & Hardin 1994).

Mercury analysis on fish tissue was done using the Environmental Protection Agency (EPA) Method 245.1, cold vapor technique (EPA 1979).

Sediments were collected at each site by taking cores along a transect running the width of the river, compositing the cores (between 5 and 10 cores depending on the width of the stream), and taking sub-samples for particle size, pesticides, mercury, and arsenic analysis. Samples for particle size analysis were delivered to the USDA NRCS Jamie Whitten Plant Materials Center Laboratory in Coffeeville, Mississippi (PMC) for analysis. Particle size analysis was done using the hydrometer method (ASTMd 1985).

Pesticide, mercury, and arsenic testing on sediments was done at MSCL. Pesticide samples were tested using methods from the FDA manual on pesticide testing (McMahon and Hardin 1994). Mercury analysis on sediments were done using the EPA Method 245.1, cold vapor technique (EPA

1979). Arsenic was determined by EPA Method 206.2, atomic adsorption, graphite furnace technique (EPA 1979).

RESULTS AND DISCUSSION

Sediments

Sediments were all classified as clays with percent clay ranging from 42 to 80 %, percent silt 12 to 30 %, and percent sand 5 to 39 % (Table 1).

Metals. There are no EPA or FDA standard levels for mercury and arsenic in sediments. There is a proposed Resource Conservation and Recovery Act (RCRA) level of 80 ppm arsenic in soils (Meister 1994). Concentrations of mercury and arsenic in the earth's crust and in virgin soils are commonly used reference points to estimate contamination since all sediments originate as soil. Sediment mercury levels ranged from 0.005 to 0.052 ppm with an average value of 0.03 ppm (Table 2). These values fall at the low end of the estimated 0.03 to 0.08 ppm levels in the earth's crust (Jonasson and Boyle 1971). Arsenic levels ranged from 1.3 to 4.3 ppm with an average value of 2.6 ppm. These values are also at the low end of the native arsenic levels in virgin soils which range from 0.2 to 40 ppm with an average of 5 ppm (Walsh & Keeney 1975) and well below the proposed RCRA value.

Pesticides. Sediments were tested for 58 pesticides (18 Nitrogen-Phosphorus pesticides, 28 organochlorine pesticides, 12 pesticides used primarily on cotton). The only pesticides detected in quantifiable amounts were DDT and its metabolites (Table 3). The most prevalent form was p,p'-DDE followed by p,p'-DDD indicating that DDT in this environment is continuing to degrade (Ware and Roan 1985). Levels for total DDT ranged from 0.01 to 0.30 ppm, average was 0.11 ppm. Sediment levels of 0.35 ppm total DDT are thought to cause moderate effects to biota (NOAA 1990). The proposed RCRA level for DDT in soil is 2 ppm, DDE 2 ppm, and DDD 3 ppm. These are all higher than the maximum level found in study samples. Since DDT is a persistent but banned pesticide, only time will eliminate it from our streams. The US Department of Health and Human Services, Food and Drug Administration (FDA), considers this pesticide to be "unavoidably present" (Hardin, personal communication).

Fish Samples

Pesticides. Fish tissue testing for 58 pesticides (18 Nitrogen-Phosphorus pesticides, 28 organochlorine pesticides, 12 pesticides used primarily on cotton) resulted in detection of quantifiable amounts of 9 organochlorine pesticides, chlordane, 4 forms of DDT, dieldrin, pendimethalin, toxaphene, and trifluralin (Figure 2).

FDA has not set action levels for all pesticides that might be found in fish tissues because there are inadequate data from which to work. A frame of reference to determine if levels of pesticides in fish samples from the Mississippi Delta or different from levels found in fish from other parts of the United States was needed to estimate anthropogenic effects. The National Contaminant Biomonitoring Program (NCBP) data (Schmitt et al. 1990) provides this reference for comparison based on testing a total of 321 composite fish samples from 112 stations throughout the nation for organochlorine pesticides. Comparisons do not provide judgments about the effects of levels of pesticides in fish, but do give us an idea of the extent of contamination in the Delta compared to other regions.

The NCBP data are presented as ranges and geometric means. Geometric means are used to replace arithmetic means to minimize the effects of outlying values. Therefore, geometric means of this study data were calculated. An estimate of 75% of the detection limit was used to replace zero values (Conzelmann et al. 1995).

Chlordane was found in 3 of the study fish tissue samples, with an average level of 0.01 ppm and a geometric mean of 0.001 ppm. The geometric mean is much less than the arithmetic average in this case because all 41 samples are included in calculating geometric mean and the average is of only the 3 samples containing chlordane. A geometric mean chlordane level of 0.03 ppm was reported for the NCBP data. Chlordane was widely used for insect control over a 40 year period. It was limited to termite control only from 1983 to 1988 when it was banned from any use in the United States. Levels should continue to decline as the fish population ages because there were no quantifiable levels of chlordane in sediment samples leaving predation as the primary source for bioaccumulation.

Total DDT (the sum of metabolites plus parent compound) was found in all 41 fish tissue samples ranging from 0.12 to 7.05 ppm with an average of 1.44 ppm and geometric mean of 0.98 ppm. The NCBP range for total DDT was below the limit of detection (BLD) to 9.08 ppm with a geometric mean of 0.26 ppm. Study samples were within the reference range but exceeded the reference geometric mean. The Delta total DDT maximum value was less than other parts of the nation, but there were apparently more individual higher values than in the NCBP data, producing the higher geometric average. Although use of DDT has been banned since 1973, past use in this area is still evident in these samples. However, all of the fillet samples tested were well below FDA's 5.0 ppm action level for total DDT in fillets.

Dieldrin was found in 26 samples ranging from 0.01 to 0.04 ppm with an average of 0.01 ppm and geometric mean of 0.005 ppm. The NCBP range for dieldrin was BLD to 1.39

ppm with a geometric mean of 0.04 ppm. Samples in this study were at the low end of the reference range and the maximum level found was equal to the reference geometric mean. FDA has set an action level of 0.3 ppm in tissue. These samples were well below that level. Dieldrin levels in Delta samples were very low when compared to NCBP data indicating a declining influence of this pesticide.

Pendimethalin is considered to be slightly toxic to humans and is readily removed as body waste. It was found in 19 samples ranging from 0.02 to 0.45 ppm with an average of 0.04 ppm and geometric mean of 0.005 ppm. There are no NCBP data. Toxicological data for rats indicate an LD_{50} of > 8000 ppm (Meister 1994).

Toxaphene was found in 39 samples ranging from 0.13 to 5.2 ppm with an average value of 1.38 ppm and a geometric mean of 0.66 ppm. The NCBP range for toxaphene was BLD to 8.2 ppm. Samples from this study were at the low end of this range, but the geometric mean is higher than the NCBP geometric mean value of 0.14 ppm. As with total DDT, the Delta toxaphene maximum value was less than other parts of the nation, but there were apparently more individual higher values than in the NCBP data, producing the higher geometric average. Although use of toxaphene has been banned since 1983, past use in this area is still evident in these samples. However, all of the fillet samples tested were well below FDA's 5.0 ppm action level for toxaphene in fillets.

Trifluralin, currently a widely used herbicide, was found in 22 samples ranging from 0.01 to 0.09 ppm, with an average of 0.015 ppm and a geometric mean of 0.004 ppm. Trifluralin is considered to be nontoxic to moderately toxic to humans. Toxicological data for rats indicate an LD_{50} of > 10,000 ppm (Meister 1994).

Metals, Whole Fish. Maximum, minimum, and average levels of mercury for all 41 fish samples, tested as both whole fish and fillets, are reported in Figure 3. Mercury levels in 19 channel catfish ranged from 0.07 to 1.00 ppm, with an average value of 0.36 ppm and a geometric mean of 0.26 ppm. Levels in 5 bullhead catfish ranged from 0.12 to 0.57 ppm, with an average value of 0.37 ppm and a geometric mean of 0.32 ppm. Levels in 7 blue catfish ranged from 0.10 to 0.47 ppm, with an average value of 0.23 ppm and a geometric mean of 0.20 ppm. Levels in 2 flathead catfish ranged from 0.24 to 0.59 ppm, with an average value of 0.42 ppm and a geometric mean of 0.38 ppm. Only one whole fish was at the FDA recommendation for maximum mercury level of 1.00 ppm. This level was set, as a safety margin, at one-tenth the lowest level of mercury documented to cause some reaction in humans, including headache, dizziness, any symptom.

Metals, Fillets. Fillet levels of mercury may be higher than whole fish levels because mercury binds strongly to muscle tissue. Maximum, minimum, and average levels of mercury for fillet samples are reported in Figure 3. Levels in 13 channel catfish fillets ranged from 0.14 to 0.99 ppm, with an average value of 0.48 ppm and a geometric mean of 0.37 ppm. Levels in 2 bullhead catfish fillets ranged from 0.55 to 0.57 ppm, with an average value of 0.56 ppm and a geometric mean of 0.56 ppm. Levels in 3 blue catfish ranged from 0.16 to 0.27 ppm, with an average value of 0.21 ppm and a geometric mean of 0.21 ppm. No flathead catfish fillets were tested. Three channel catfish fillets were at 0.99 ppm, virtually at the FDA recommendation for maximum mercury level of 1.00 ppm.

CONCLUSIONS

Metals. Sediment mercury and arsenic concentrations are not at problem levels, indicating no current large anthropogenic inputs. Four catfish samples were at or near the FDA mercury action level.

Pesticides. Sediment levels of DDT and its metabolites were lower than standards set for soils or sediments. No catfish fillet exceeded the FDA action levels for DDT or toxaphene. Fish levels for chlordane and dieldrin were low compared to NBCP levels. Levels of pendimethalin and trifluralin were below any level that could produce a toxic effect in rats.

Examination of all samples in this study by comparison to established limits did not reveal any significant health risk to people relying on subsistence fishing in the Mississippi Delta.

ACKNOWLEDGMENTS

This work would not have been possible without the cooperation of USDA NRCS Area 4 employees, Pam Morris and Reggie Liddell (Clarksdale, DC Kent Blaine), Willie Terry (Tunica Soil Survey), Johnny Hancock (Greenwood area office), and Paul Rodrigue (Delta Water Resources) who all helped collect the samples under the direction of Gerald Clark (Tunica, DC Ken Oatis, who also helped in the boat!). I particularly want to thank Gerald Clark, for an excellent job in organizing and implementing this effort. I appreciate the advice of Miller Beard, LeFlore County, who helped get this effort started by saying "If it swims in Mississippi, Gerald Clark knows the best way to catch it." None of this would have been possible without the blessing of James Johnson, Area Conservationist and the cooperation of Kent Blaine (Clarksdale) and Ken Oatis (Tunica), DCs.

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Table 1 . Sediment Particle Size Analysis.

Sample Location	Clay	Silt	Sand
		Percent	
Coldwater River, Brahan Road, site 11	67	24	9
Yazoo Pass, Rich, site 10	42	30	28
Mill Creek, Dog Bog Road, site 12	59	20	21
Sunflower River Farrel-Eagle Nest RD, site 13	62	22	16
Sunflower River, Dulaney, site 14	45	16	39
Bogue Phalia, between sites 15 and 16	53	24	23
Quiver River, Drew, Hoard Road, site 17	79	12	9
Quiver River, Parchman, Hwy. 32, site 18	54	22	24
Deer Creek, Leland, site 2	80	15	5
Deer Creek, Cary, site 6	70	25	5

Table 2. Sediment Metal Analysis.

Sample Location	Mercury	Arsenic
	ppm	
Coldwater River, Brahan Road, site 11	0.050	1.3
Yazoo Pass, Rich, site 10	0.030	3.0
Mill Creek, Dog Bog Road, site 12	0.005	2.0
Sunflower River Farrel-Eagle Nest RD, site 13	0.035	1.8
Sunflower River, Dulaney, site 14	0.033	2.5
Bogue Phalia, Hwy. 32, site 15	0.045	3.8
Bogue Phalia, Hwy. 446, site 16	0.023	1.8
Quiver River, Drew, Hoard Road, site 17	0.052	4.3
Quiver River, Parchman Hwy. 32, site 18	0.030	2.5
Deer Creek, Leland, site 2	0.033	2.8
Deer Creek, Cary, site 6	0.005	2.3
Average	0.030	2.6

Table 3 . Sediment Pesticide Analysis.

Pesticide	o,p'-DDD	o,p'-DDE	o,p'-DDT	p,p'-DDD	p,p'-DDE	p,p'-DDT	Total
Sample Location				ppm			
Coldwater River, site 11	0.02	0.01	0.01	0.08	0.08	0.03	0.23
Yazoo Pass, site 10	ND	ND	ND	ND	0.02	0.02	0.04
Mill Creek, site 12	ND	ND	ND	0.02	0.02	0.01	0.05
Sunflower River, site 13	0.01	0.01	*ND	0.07	0.10	0.02	0.21
Sunflower River, site 14	ND	ND	ND	0.02	0.02	ND	0.04
Bogue Phalia, site 15	0.02	0.01	ND	0.05	0.07	0.01	0.13
Bogue Phalia, site 16	ND	ND	ND	0.02	0.04	0.01	0.07
Quiver River, site 17	0.01	0.01	ND	0.10	0.15	0.03	0.30
Quiver River, site 18	ND	ND	ND	ND	0.01	ND	0.01
Deer Creek, site 2	ND	ND	ND	0.01	0.01	ND	0.02
Deer Creek, site 6	0.01	ND	ND	0.03	0.09	0.03	0.16

*ND = None Detected

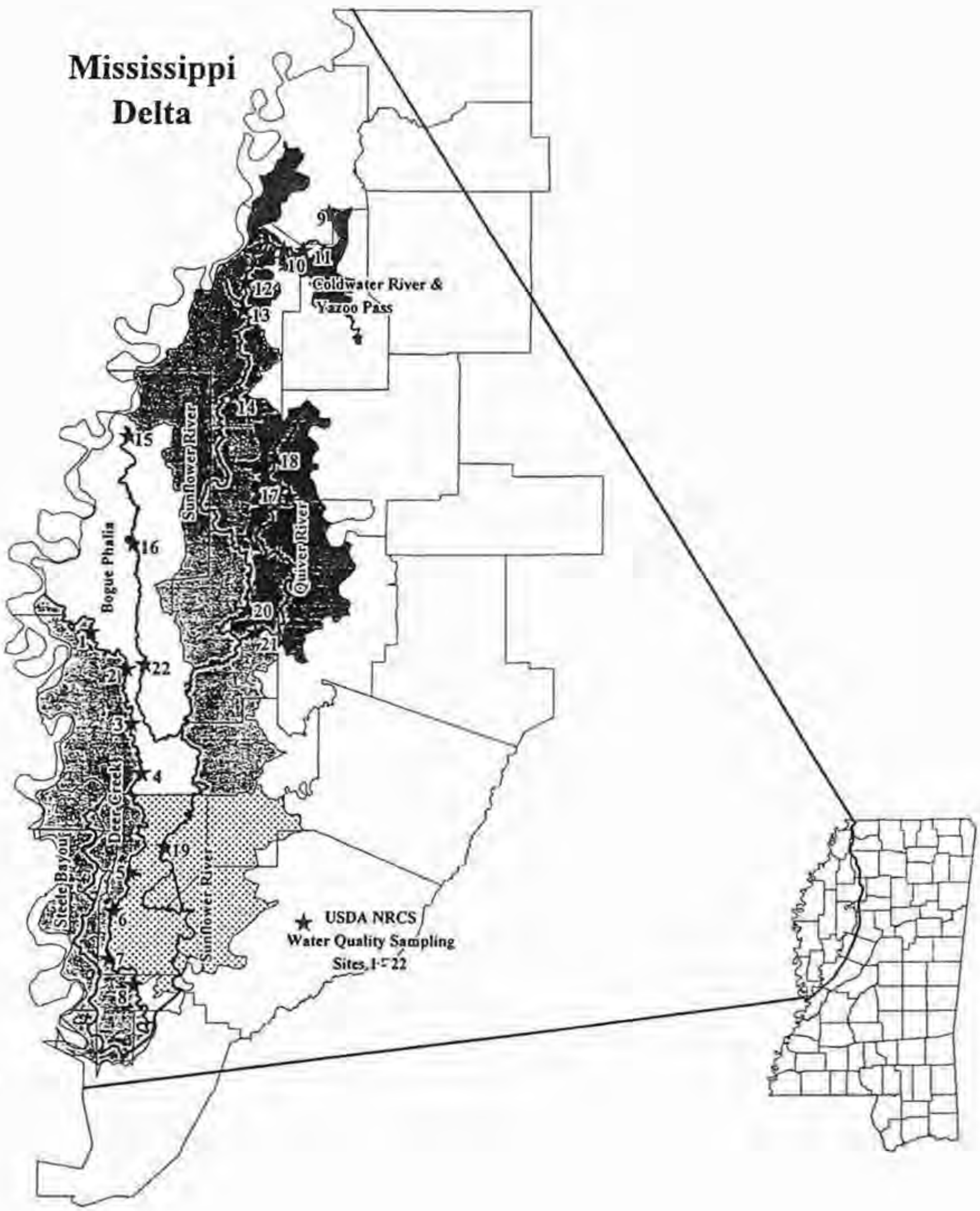


Figure 1. Sampling sites for the Mississippi Delta Water Supply Study (water, sediment, and fish). Shaded areas are the major watershed boundaries.

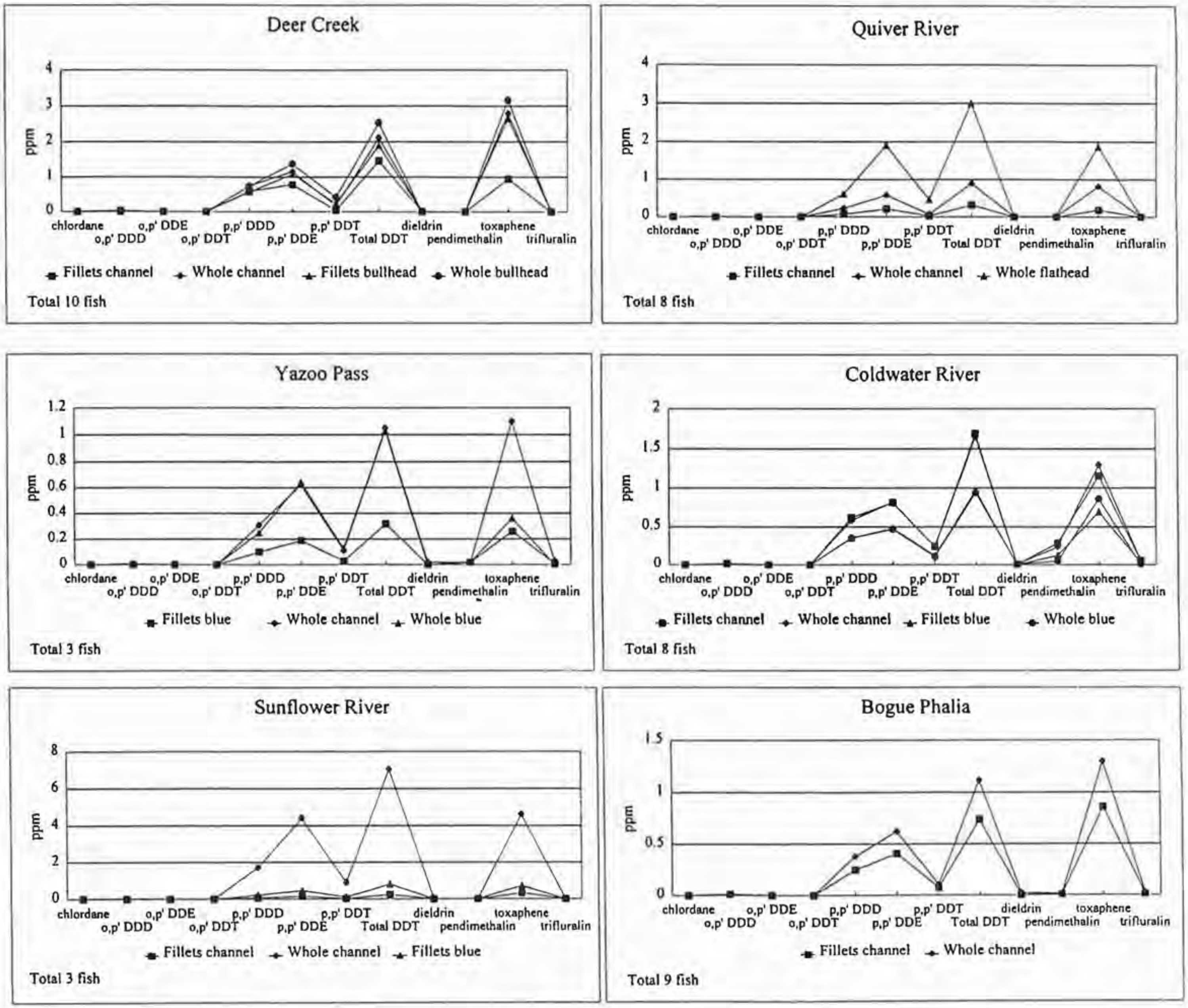
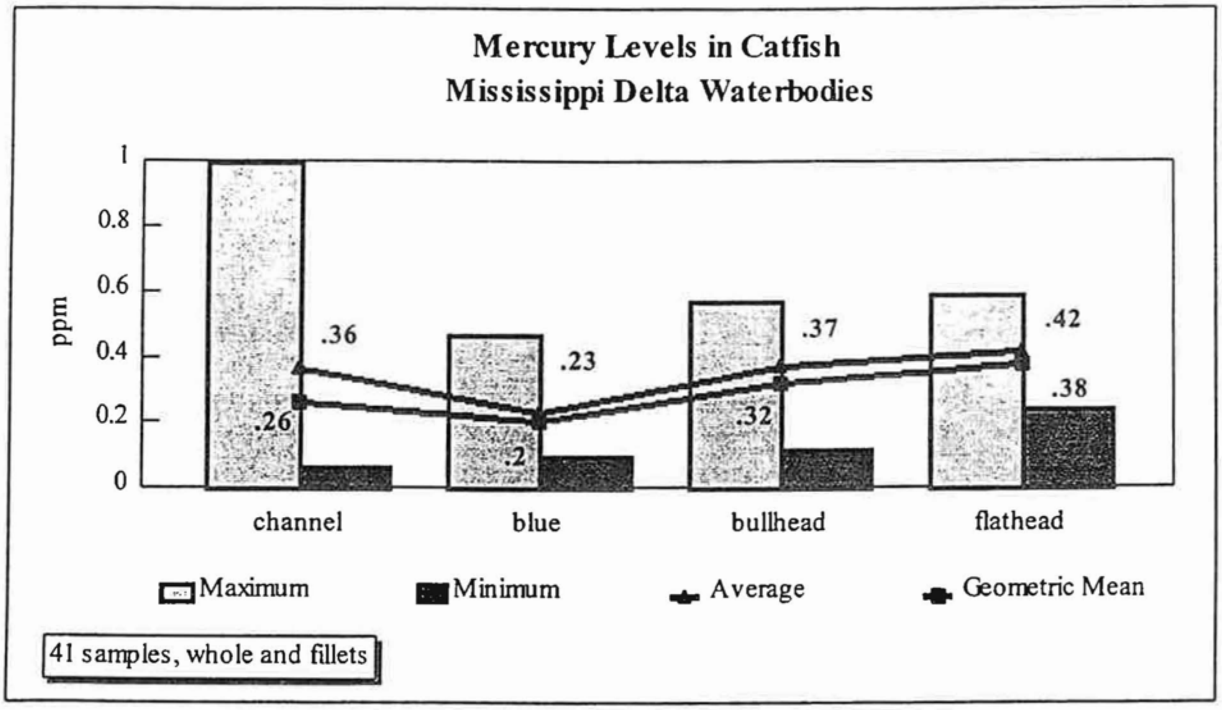


Figure 2. Organochlorine pesticides in fish samples from the Delta Water Supply Study by waterbody.



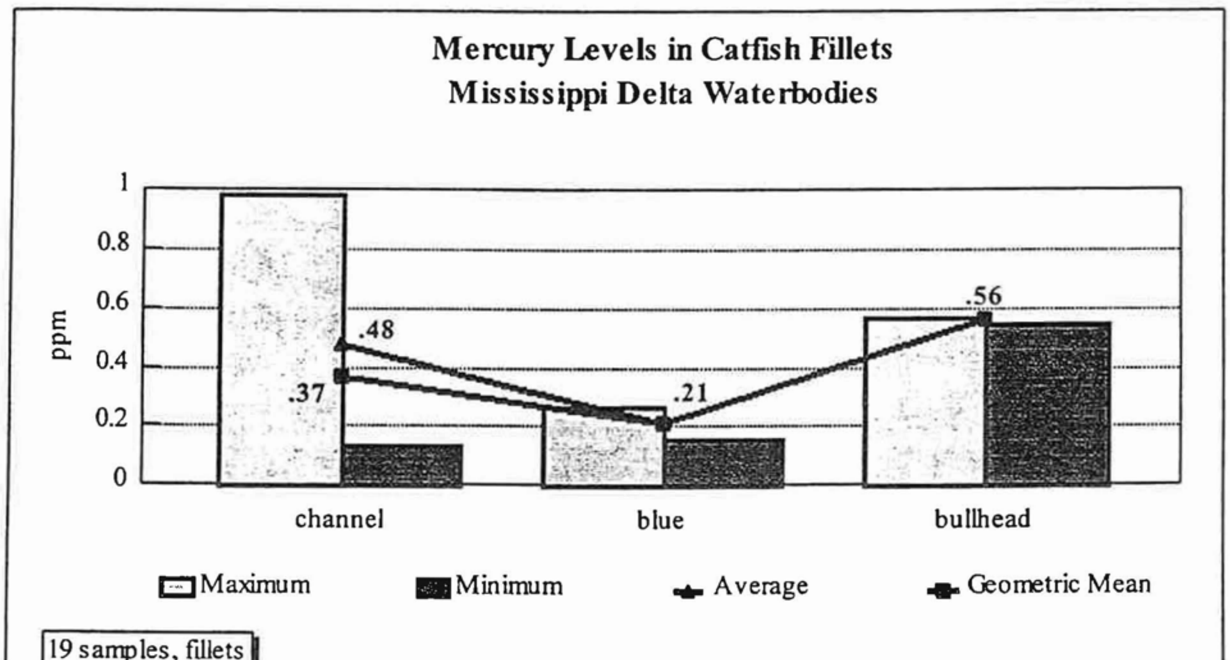


Figure 3. Top graph: Maximum, minimum, average and geometric mean mercury levels in all fish samples, whole fish and fillets, in the Delta Water Supply Study. Bottom graph: Maximum, minimum, average and geometric mean mercury levels in fillet portions only.