Residues of Mirex and Other Chlorinated Pesticides in Commercially Raised Catfish

by

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In the United States, in excess of 95% of the insecticide mirex is used for control of the imported fire ant in nine southeastern States (1). This insecticide is broadcast applied at the rate of 1 1/4 lbs/acre (1.7 grams actual toxicant) over pastures and fields infested by this pest. In monitoring studies conducted in areas where this pesticide has been extensively used, very small residues of mirex have been detected in a large variety of nontarget organisms (1). Mirex also has been detected in wild catfish from areas where large scale control programs have been conducted (Table 1).

In the Southeast, particularly the State of Mississippi, the rearing of catfish in artificial ponds has become a major industry that presently exceeds a hundred million dollars a year.

Table 1. Mirex residues in wild catfish from areas having received blanket applications of mirex bait, including marshes, streams and ponds.

Location	Time Since Last Treatment	Number Fish Sampled	Mirex Residues (PPM)
Harrison County, Miss.* (small area-2,000 acres)	48 hrs	5	2.59
	3 wks	10	.31
	2 mos	5	.11
	1 yr	10	.084
	2 yrs	5	.019
Oktibbeha Co., Miss. (large area-200,000 acres)	3 mos	5	.45
	6 mos	5	.25
Pinellas Co., Fla. (entire county treated)	1 yr	3	.019
	2 yrs	3	.013
Savannah, Georgia (several million acres)	1 yr	3	.026
	2 yrs		.008

* Marine catfish from estuary in treated marsh.

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The purpose of this study was to sample and analyze commercially raised catfish from parts of Mississippi and southern Arkansas in which the insecticide mirex has been used extensively for the control of the fire ant. It was hoped to learn what levels of residues could be expected and how widespread was their occurrence. While no specific tolerance level has been set for catfish, the present tolerance level for fat of farm animals is 0.1 ppm and raw agricultural products 0.01 ppm (2). At the time of writing, the Food and Drug Administration (FDA) had not set an action guideline for mirex but the action guideline for maximum permissible concentration for the related organochlorine pesticides, i.e., endrin and the combination of aldrin and dieldrin, in the edible portion of fish is not to exceed 0.3 ppm.

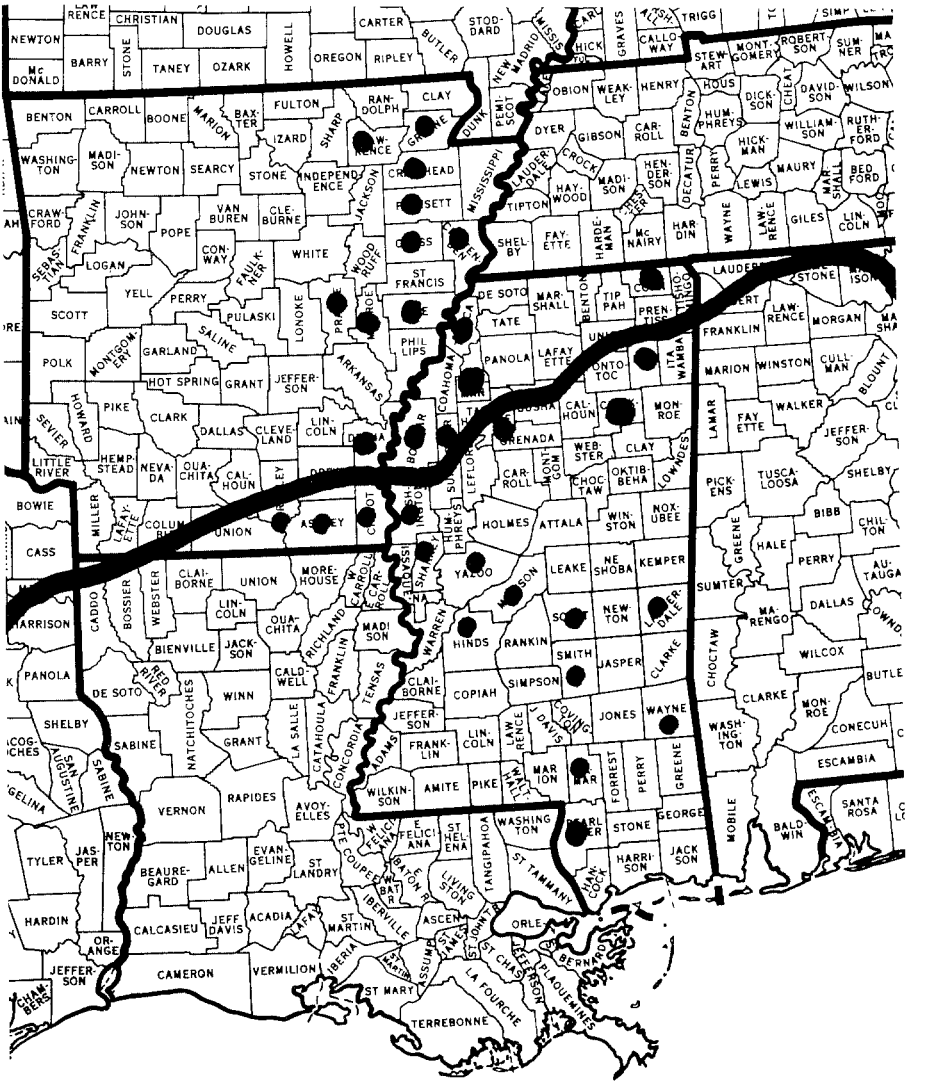
In developing techniques for monitoring mirex in the past three years, our laboratory has found two possible sources of error (1). First, the PCB Aroclor 1260 is frequently found in aquatic and marine samples and can be confused with mirex. Secondly, mirex is sold under another trade name, Dechlorane, by Hooker Chemical Company as a fire retardant, and therefore unknown amounts of this chemical could be entering the environment by discarded manufactured goods. With these two points in mind, it was decided to double the number of samples by collecting an equal number from various points in north Mississippi and Arkansas where the imported fire ant is not found and therefore mirex, the insecticide, has never been used. These would be used as a check and if residues were detected in these samples, it could be presumed that these were not insecticide but were either a PCB or Dechlorane. These residues could be then averaged to give a baseline to which the samples collected from within the infested area could be compared. Samples found containing mirex in excess of this baseline level could be presumed to contain mirex which had been applied for fire ant control.

It was also felt to be worth the little extra effort needed to run the samples for other chlorinated pesticides to be able to present a more complete residue picture for catfish.

Methods and Materials

Sample Collection: Samples to be used had all been collected as part of a cooperative USDA/USDI Bureau of Commercial Fisheries study on catfish production in the Southeast. In the spring of 1970, USDA PPD field inspectors had collected samples of catfish, catfish food, sediment and water from several hundred catfish ponds in the Southeast. These samples were split between Department of Interior laboratory in Stuttgart, Arkansas, and the USDA laboratory at Gulfport, Mississippi, for analysis. For this study, 25 catfish samples were selected and analyzed for mirex and other pesticides. Seven of the samples chosen came from areas which had received a county-wide total coverage treatment and therefore had probably received mirex directly on the water of the catfish pond. The remainder of the samples were chosen from those areas where the fire ant is known to be a pest and mirex is exten-

Fig. 1. Maps of Mississippi and Arkansas, showing location where catfish samples were collected. The heavy diagonal line represents the present approximate range of the imported fire ant.



sively used by farmers and homeowners for its control. Twenty-five additional samples were chosen from north Mississippi or Arkansas, all beyond the present range of the imported fire ant, to be used as checks.

The locations of counties from which samples were taken are shown in Fig. 1. In some places two or more ponds were sampled if that county was found to be a major producer of catfish. Each sample came from a commercial pond, one in which farmers were raising the catfish as a crop by introducing fingerling size catfish in spring or summer and feeding them through the fall and winter on

artificial food until they were marketed the following year (3). Each sample consisted of 2 or 3 fish of marketable size, 1 to 1 1/2 lbs in weight, and were usually purchased from the owners of the catfish ponds. Samples were frozen in dry ice and shipped to Gulfport, Mississippi, for analysis.

Sample Cleanup: Originally it had been planned to sample only the fat from the catfish, since this would contain the highest residues of mirex and other pesticides. However, in examining the catfish it was found that they varied considerably in the amount of fat they contained and would not produce comparable samples. Instead, fish were analyzed on edible portion, that is, the meat which would be normally marketed and consumed by humans.

Cleanup Procedure: The catfish were skinned, gutted and beheaded for analysis. Edible portion of the 2 or 3 fish was ground in a Hobart food chopper, a 20 gram subsample was placed in an explosion-proof Waring blendor with 500 ml of 3:1 mixture of hexane-isopropyl alcohol, blended for 2 to 3 minutes, transferred to a jar on a concentric rotator and mixed for two hours. A 300 ml aliquot was then taken from the sample (this represented 15 grams of the original fish) filtered through prewashed glasswool and the isopropanol washed out with water. The final solution was dried by filtering through anhydrous sodium sulfate. The final extract was concentrated to 45 ml and 2-15 ml aliquots (each representing 5 grams of the original fish) were taken for cleanup. The remaining 15 ml sample was stored in the event future analysis was needed.

One of the 15 ml aliquots was partitioned through acetonitrile by adding 35 ml hexane to the sample, making a total of 50 ml, and then mixed with equal volume of acetonitrile saturated with hexane and partitioned. Partitioning with acetonitrile was repeated 3 times. Next the acetonitrile solution was dried by filtering it through sodium sulfate column, concentrated to 15 ml and hexane added to return the sample to 50 ml. This process was repeated twice to insure complete removal of acetonitrile. The final 15 ml of hexane solution was put through Florisil column and concentrated, and was ready for analysis.

This fraction was analyzed for chlorinated pesticides DDT, toxaphene, aldrin, dieldrin, endrin, chlordane, etc. The second 15 ml subsample was extracted with hexane, cleaned up with a concentrated sulfuric acid wash, fractionated or a Florisil column and analyzed for mirex. This cleanup procedure has been described elsewhere (1). Sensitivity for mirex and other pesticides was determined to be 0.01 ppm.

GLC Analysis: Two columns were used for analysis. The first was a mixture of 1.5% OV-17 and 1.95% QF-1 on Gas Chrom Q and temperatures of: injector - 250°C; oven 200°C; detector - 210°C. The second column was 3% DC 200 on Gas Chrom Q with injector temperature of 245°C; oven temperature of 175°C; and detector temperature of 205°C. Argon-methane at 1-0 ml/min was the carrier gas. These two methods of analysis gave 90-100% recovery when the sample was fortified with mirex or one of the other pesticides and taken through

Table 2. Residues of mirex and other chlorinated hydrocarbon pesticides detected in commercially raised catfish. Sites were located in counties where the IFA is found and where mirex would be used for its control. Residues expressed as parts per million on whole body weight of 2 or 3 fish per site. Level of sensitivity .01 ppm; n.d. indicates not detected. Sites are identified by County.

Location	DDT*	Toxaphene	Dieldrin	Endrin	Aldrin	Chlordane	Heptachlor Hept. Epoxide	Mirex
Mississippi								
Chickasaw	0.47	0.63	0.02	0.03	nd	nd	nd	nd
Hinds	0.22	1.31	nd	nd	nd	nd	nd	nd
Lamar	0.24	0.24	0.01	nd	nd	nd	nd	nd
Lauderdale	0.15	nd	nd	nd	nd	nd	nd	nd
Lee #1	0.19	0.40	0.02	0.02	nd	nd	nd	nd
Lee #2	0.36	0.57	0.03	0.01	nd	nd	nd	nd
Madison	1.66	1.44	0.03	0.03	nd	nd	nd	nd
Pearl River	0.13	0.17	0.01	nd	nd	nd	nd	nd
Scott	1.29	3.23	0.04	0.04	nd	nd	nd	nd
Sharkey	0.47	1.23	0.01	0.03	nd	0.40	nd	nd
Smith	0.17	0.20	nd	nd	nd	nd	nd	nd
Tallahatchie	1.50	2.97	0.03	0.02	nd	nd	nd	nd
Warren	0.27	0.35	0.01	nd	nd	nd	nd	nd
Washington #1	4.15	2.79	0.01	0.03	nd	nd	nd	nd
Washington #2	1.25	0.78	0.01	nd	nd	nd	nd	nd
Washington #3	1.07	2.63	0.87	0.11	nd	nd	nd	nd
Washington #4	1.79	4.10	0.08	0.09	nd	nd	nd	nd
Washington #5	8.71	16.74	0.08	0.23	nd	nd	nd	nd
Wayne	0.87	0.80	0.01	0.03	nd	nd	nd	nd
Webster	0.83	0.38	0.01	0.01	nd	nd	nd	nd
Yazoo	0.30	0.50	0.14	0.02	nd	nd	nd	nd
Arkansas								
Ashley #1	1.10	2.49	0.02	0.02	nd	nd	nd	nd
Ashley #2	1.68	3.05	0.08	0.06	nd	nd	nd	nd
Bradley	0.43	0.18	nd	nd	nd	nd	nd	nd
Chicot	1.99	1.72	0.03	0.04	nd	nd	nd	nd

*Values include p,p'DDE, p,p'TDE and o,p'DDT

Table 3. Residues of mirex and other chlorinated hydrocarbon pesticides detected in commercially raised catfish. Collection sites were located in counties in which the IFA has never been found so mirex has probably never been used. Residues expressed as parts per million on whole body weight of 2 or 3 fish per site. Level of sensitivity .01 ppm; n.d. indicates not detected. Sites are identified by County.

Location	DDT*	Toxaphene	Dieldrin	Endrin	Aldrin	Chlordane	Heptachlor Hept. Epoxide	Mirex
Mississippi								
Alcorn	0.09	0.23	0.01	0.01	nd	nd	nd	nd
Bolivar #1	3.22	4.05	0.07	0.16	nd	nd	nd	nd
Bolivar #2	1.42	2.25	0.03	0.38	nd	nd	nd	nd
Bolivar #3	0.21	0.26	nd	nd	nd	nd	nd	nd
Quitman	2.35	1.56	0.21	0.10	nd	nd	nd	nd
Sunflower	2.97	8.95	0.17	0.27	nd	nd	nd	nd
Tunica	0.78	2.01	0.01	nd	nd	nd	nd	nd
Arkansas								
Craighead	0.32	0.48	0.03	nd	nd	nd	nd	nd
Crittendon	0.43	1.02	0.09	0.02	nd	nd	nd	nd
Cross #1	0.23	nd	0.11	nd	0.01	nd	nd	nd
Cross #2	0.38	0.66	0.05	0.01	nd	nd	nd	nd
Desha	1.02	20.67	0.03	0.09	nd	nd	nd	nd
Greene	0.17	0.24	0.39	nd	nd	nd	nd	nd
Lawrence	0.29	0.37	0.03	0.01	nd	nd	nd	nd
Lee	0.64	0.91	0.04	0.06	nd	nd	nd	nd
Lincoln #1	0.60	0.86	0.32	0.41	0.03	nd	nd	nd
Lincoln #2	3.45	0.95	0.01	0.04	nd	nd	nd	nd
Lincoln #3	0.45	0.53	0.02	0.03	nd	nd	nd	nd
Lincoln #4	0.51	0.38	0.04	0.03	0.01	nd	nd	nd
Monroe	0.35	0.94	0.03	0.13	nd	nd	nd	nd
Poinsett #1	0.63	0.70	0.03	0.02	nd	nd	nd	nd
Poinsett #2	0.36	0.85	0.06	0.01	nd	nd	nd	nd
Poinsett #3	0.23	0.25	0.14	nd	nd	nd	nd	nd
Poinsett #4	0.30	0.41	0.11	0.02	nd	nd	nd	nd
Prairie	0.50	0.93	0.05	0.03	nd	nd	nd	nd

*Values include p,p'DDE, p,p'TDE and o,p'DDT

the complete procedure. A Hewlett Packard Model 402 with electron capture was used for analysis.

Results and Discussion

The results of the analyses of the 25 samples from areas where mirex was being used are shown in Table 2. The remaining 25 samples from check areas in Arkansas and northern Mississippi are shown in Table 3. Mirex was found in none of the 50 samples at the detection level, 0.01 ppm. However, all samples from both areas contained extensive residues of other pesticides. DDT and its analogs (p,p'DDE; p,p'TDE; and o,p'DDT) were found in all samples and averaged 1.64 ppm. Toxaphene was found in 96% of the samples and averaged 1.98 ppm. Dieldrin was found in 90% of the samples and averaged .07 ppm. Endrin found in 76% of the samples averaged .05 ppm, aldrin in 6% of the samples, chlordane in one sample and heptechlor or heptachlor epoxide in none of the samples. PCB's were suspected in many of the samples but were not confirmed. The high residues of DDT and toxaphene are probably the result of a large majority of the catfish ponds sampled being in the delta region of Mississippi which is also a major cotton growing region. Toxaphene and DDT are still extensively used in this area to control cotton insects (4).

The lack of detectable mirex residues in any samples analyzed would indicate that there was not widespread contamination of the catfish. Conversely, it would appear that mirex is probably one of the least of the chlorinated pesticides to reach humans by consumption of catfish. It is also doubtful that the residues could be responsible for the deformation or death of fish. In the major study of the effect of mirex on fish (5) gill deformity, kidney lesions, and retarded growth resulted from exposure to mirex. However, the dosages of mirex used were up to several thousand times that normally applied in the field and then were applied directly to the fish ponds. The whole body residues of the affected fish usually were in the range of 100 ppm. Lower dosages producing residues of less than 1 ppm showed no noticeable effects. It can therefore be concluded that if mirex residues did occur in the catfish sampled, they were less than 10 ppb. This means that a safety factor exists between what might have existed in the field samples examined and what could be expected to produce adverse effects of almost 1,000 times.

References Cited

1. MARKIN,G.P., J.H. FORD, J.C. HAWTHORNE, J.H. SPENCE, J.R. DAVIS, and C.D. LOFTIS. Pesticide Monitoring Bulletin. In Press.
2. U.S. Department of Agriculture. 1969. Summary of Registered Agricultural Pesticide Chemical Uses. Mirex III-D-45.
3. Mississippi State University Extension Service. Production of Channel Catfish. Publication 622.
4. U.S. Department of Agriculture, 1968. Agricultural Handbook No. 331.
5. VAN VALIN, C.C., A.K. ANDREWS and L.L. ELLER. 1968. Trans. Amer. Fisheries Soc. 97: 185-196