Changes in Dieldrin and $p,p'$-DDE Residues Following Cooking of Channel Catfish

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ABSTRACT

The influence of cooking (frying, baking, and smoking) on dieldrin and 1,1-dichloro-2,2-bis[4-chlorophenyl]ethylene (DDE) residues in treated channel catfish (Ictalurus punctatus) was determined. Dieldrin and DDE were significantly reduced ($P < 0.05$) during cooking of catfish by 50 to 65% (dry basis) and 50 to 80%, respectively. Smoking resulted in maximum reduction (82%) of DDE residues, while baking resulted in the least reductions for both dieldrin (50%) and DDE (50%) when compared to the other preparation methods.

Key words: Catfish, cooking, pesticides, dieldrin, DDE

In recent years, fish and other aquatic foods have gained popularity among American consumers (1). Fish, a good source of protein and often low in fat, has attracted consumers due to health benefits (1). Farm-raised channel catfish is the fourth most popular fish in the U.S., following tuna, cod, and pollock (3). Per capita consumption in 1990 was 0.34 kg and by 1992 it increased by almost 23%, to 0.41 kg. While the three most popular fishes are marine species, catfish is the main freshwater fish consumed in U.S., and therefore, it has the greatest potential for delivering environmental contaminants found in fresh water to consumers. The reports of organochlorine residues primarily in recreational fishes has resulted in consumer concern over the safety of fish (5). Since the levels of these residues are known to be greatly influenced by the preparation of fish before consumption (4, 7, 8, 10, 15), it is pertinent to investigate the actual effects of cooking on specific residues present in catfish.

A number of studies have been conducted to evaluate the effects of cooking on chemicals like DDT, polychlorinated biphenyls, dieldrin, mirex, etc., in fish (4, 9, 10, 15, 16). These reports indicate a large reduction in pesticide residues during normal processing and cooking. However, these reports also suggested that residue reduction was found to be dependent on fish species and specific residue; hence, it was necessary to investigate whether similar reductions could be obtained for selected organochlorine residues in channel catfish. The influence of three common cooking methods on two organochlorine compounds, DDE and dieldrin, was studied. The cooking methods included frying (two processes), baking, and smoking, which are commonly employed in catfish preparation at home, in restaurants, and in commercial processing operations (1, 6).

MATERIALS AND METHODS

Channel catfish were raised with 18 fish (15 kg) in each tank (tank volume, 10.22 m$^3$; the water was exchanged five times during the study). The fish in two tanks were fed each residue. The fish were fed a floating catfish feed (Alabama Farmers Cooperative Inc., Decatur, AL) for a period of 25 days at the rate of 1% of body weight and then at a rate of 0.5% for the next 13 days in order to maintain water quality. Feed composition was 32% protein, 2.5% fat, 6.0% fiber, and 12.0% moisture. Dieldrin (Sigma Chemical Co., St. Louis, MO) and DDE (Aldrich Chemical Co., Inc., Milwaukee, WI) were incorporated into feed at 4 mg kg$^{-1}$ and 5 mg kg$^{-1}$, respectively. Thoroughly ground feed was mixed with dieldrin or DDE and made into pellets using 3% carboxymethyl cellulose (Dow Chemical Co., Midland, MI) as a feed binder. The total amount of treated feed consumed by the fish in each tank during 38 days was 5.4 kg, which contained an average of 21.6 mg of dieldrin and 27.0 mg of DDE. A group of fish (control) were fed commercial feed with no added organochlorines.

At harvest, 24 fish for each organochlorine were collected and divided into 4 groups to be cooked using one of four methods described below. Fish were physically stunned with a heavy hammer, weighed, measured for length, beheaded using a band saw (Model 22, BIRO Manufacturing Co., Marblehead, OH), skinned using a skinning machine (TECHO, Townsend Engineering Co., Des Moines, IA), and then hand filleted into matching fillets, keeping the belly flaps intact. Matched fillets were subsequently analyzed for the chlorinated residues with one fillet being maintained raw while the other was cooked. Corresponding fillets from each fish were wrapped in aluminum foil (Reynold, Reynold Metals Co., Richmond, VA), placed in zip-lock plastic bags (Glad-Lock, First Brand Corp., Danbury, CT), and stored at $-23^\circ$C for 2 to 4 months. Fillets were then thawed at 4$^\circ$C overnight prior to cooking.

The fish samples were fried (FR) in canola oil (Crisco, Proctor & Gamble, Cincinnati, OH) in a deep fryer (Colinco Fish Cooker CC-10, Damark International, Minneapolis, MN). Breaded (House...
Autry, House Autry Mills Inc., Newton Grove, NC) fillets were fried at 190°C for about 7 to 10 min until golden brown and an internal temperature of 71°C was obtained. In a variation on the frying method (IF), fillets were injected with a 6% polynaphosphate solution (Lon-O-Fos®98, Rhone-Poulenc Basic Chemical Co., Shelton, CT) to add not more than 10% to the weight of the fillet. Injected samples (IF) were stored at −23°C for four weeks, breaded, and fried as previously described. Samples were baked (BK) at 190°C (CPS 127, 27-in. (68.58 cm) single electric oven, Dacor, Pasadena, CA) for approximately 45 min until golden brown. Prior to smoking (SK), fillets were soaked in a 25% salt solution (NaCl, SX0420-3, EM Science, Gibbstown, NJ) at 10°C for about 1 h and air dried before smoking (140°C wet bulb, 160°C dry bulb for 1 h, and then 180°C wet bulb, 200°C dry bulb for 1 h). Smoke was fed for the first 30 min and total smoking time was about 2 h. All cooked fillets were packaged as before and stored at −23°C for 1 to 3 months.

Individual fillets were ground twice with using a meat grinder (Model 31FG10, Waring Products Div., New Hartford, CT). All utensils were cleaned thoroughly with detergent (Alconox, Alconox Inc., New York, NY), rinsed with water, dried, and rinsed with 2-propanol (Baker Analyzed, J. T. Baker Inc., Phillipsburg, NJ) between each sample. The samples were placed in glass bottles and stored at −23°C. For moisture determination, 1 g of thawed sample was weighed and placed in a vacuum oven (Model 282A, IsoTemp® Vacuum Oven, Fisher Scientific, NJ) at 98°C and 1.5 in Hg (ca. 5.08 kPa) for 6 h. Change in weight during drying was used to determine percent moisture.

Dieldrin and DDE residues were analyzed using a modified AOAC multiresidue method (No. 983.21) (2). After thawing ground fish overnight and mixing, a 5-g sample was weighed into a 100-ml glass beaker and mixed with 55 g of anhydrous sodium sulfate (Baker Analyzed, ACS Reagent Grade, J. T. Baker). Samples were placed in a desiccator at room temperature for at least 12 h. The mixture was transferred into a prewashed (petroleum ether, Ultra-Resi Analyzed, J.T. Baker) 33 by 80 mm cellulose thimble (Whatman International Ltd., Madison, England), plugged with prewashed glass wool (Pyrex®, Corning Inc., Corning, NY), and extracted with a Soxhlet apparatus for at least 7 h with 250 ml of hexane (Ultra-Resi Analyzed, J.T. Baker) at a turnover rate of four to five times per h. The extract was concentrated to under 10 ml with nitrogen (Turbovap II, Zymark Corp., Hopkinton, MA) at 45°C and transferred to a tared 50-ml screw-cap centrifuge tube. The remaining solvent was evaporated under a constant flow of nitrogen for 2 h at room temperature and tubes were weighed to determine fat content.

Dieldrin or DDE was extracted from fat by liquid-liquid partitioning. The sample volume was adjusted to 15 ml with petroleum ether and partitioned three times with 30 ml of acetone-trile (Ultra-Resi Analyzed, J.T. Baker) saturated with petroleum ether, by shaking vigorously for 2 min. Each time, the acetonitrile layer was transferred into a 1-liter separatory funnel containing 850 ml of deionized (DI) water, 40 ml of saturated NaCl solution and 100 ml of petroleum ether. The residues were then partitioned back into petroleum ether, filtered through anhydrous sodium sulfate, and concentrated to about 5 ml.

For cleanup of extract, a 22-mm i.d. chromatographic column was filled with 20 g of activated (at 130°C for 24 h and cooled to room temperature) Florisil® (F-100, 30/60 mesh, Fisher Scientific, Fairlawn, NJ), topped with a 1-cm layer of anhydrous sodium sulfate. The prepared column was rinsed with 50 ml of petroleum ether and the extract was transferred onto the column. Residues were eluted by using 200 ml of 6% diethyl ether in petroleum ether followed by 200 ml of 15% diethyl ether in petroleum ether. A 400-ml fraction was collected and final volume was reduced to <5 ml by evaporation at 42°C. The volume was adjusted to 5 ml and an aliquot of the extract was transferred to 2-ml injection vials.

Samples were analyzed for dieldrin and DDE residue concentration using a gas chromatograph (Model HP-5890 Series II, Hewlett-Packard Co., Avondale, PA) equipped with an autosampler and an electron-capture detector. The sample (1 liter) was separated using an HP-5, 30 m by 530 μm column (Hewlett-Packard Co.). An isothermal temperature program was used with inlet, oven, and detector temperatures of 230°C, 220°C, and 300°C, respectively. Helium (Grade 5.0, Selox-Airco, Atlanta, GA) was used as carrier gas at a flow rate of 1.5 ml min−1 and nitrogen (Grade 5.0, Selox-Airco) was used as the makeup gas with a flow rate of 60.0 ml min−1. Standards for dieldrin and DDE were prepared from U.S. Environmental Protection Agency-certified solutions (1,000 ppm in methanol, Environmental Solutions, Inc., RTP, NJ). Quantitation was based upon peak area. Retention times for dieldrin and DDE were 6.51 and 6.32 min, respectively. Standard curves for dieldrin and DDE were prepared using concentrations of 50, 100, 150, and 200 ppb, and 25, 50, 100, and 150 ppb, respectively. The limits of detection for dieldrin and DDE, as determined at twice the noise level, were 40 ppb and 25 ppb, respectively. Recoveries for both dieldrin and DDE were obtained using spiked fish samples (50, 100, and 150 ppb) in duplicate and ranged from 85 to 95%.

Statistical analysis was performed using Stavtsview 4.02 software. One-way analysis of variance with Fisher protected-LSD (p-LSD) test at 95% significance level was used to determine significant differences between treatment means.

**RESULTS AND DISCUSSION**

The results of organochlorine analysis of raw and cooked fish fillets are summarized in Tables 1 and 2. On a dry basis (db), reductions in dieldrin and DDE residues during cooking ranged from 48 to 65% and 50 to 82%, respectively. The average concentrations of dieldrin and DDE reported on a dry basis (db) in raw fillets were 637.5 ppb and 473.8 ppb, respectively. Variations in residue concentration in the fish can be attributed to differences in size, fat content, and individuality of each fish (based upon their consumption, absorption, excretion, and metabolism of the residues). Filleting technique may also be a significant source of variation due to the amount of high-fat belly-flap tissue recovered during filleting. Average moisture content in raw fish was 75.9% and was reduced to 62.8% as a result of cooking. The percent reduction obtained for dieldrin on a wet basis (wb), dry basis (db), and fat basis (fb) was 38.1, 59.4, and 57.1%, irrespective of the cooking method. In the case of DDE, the average reduction was 46.1% (wb), 65.0% (db), and 58.6% (fb). Reductions in the levels of dieldrin and DDE were significant (P < 0.05) regardless of the basis on which the results were expressed (i.e., wb, db, or fb).

Zabik et al. (15) have reported that broiling, baking or roasting, and microwave cooking significantly reduced the concentration of PCBs, dieldrin, and DDT in lake trout on a wet-weight basis and that reductions were significant when the contaminant concentrations were expressed on a percent fat basis. They heated fish to an internal temperature of 75°C, except for microwave-cooked fish, which were heated for 1 min, and reported reductions (fb) of 26 to 70% for PCB, 25 to 57% for dieldrin, and 30 to 57% for DDT in lake
TABLE 1. Dieldrin residues in six raw and cooked fish fillets from dieldrin-fed catfish prepared by frying, baking, or smoking or analyzed raw

<table>
<thead>
<tr>
<th>Parameter catfish fillet</th>
<th>Moisture (%)</th>
<th>Fat (%)</th>
<th>Wet basis</th>
<th>Dry basis</th>
<th>% fat basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dieldrin (ppb) mean ± SD (n = 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooking method</td>
<td>Length (cm)</td>
<td>Weight (g)</td>
<td>Raw</td>
<td>Cooked</td>
<td>Raw</td>
</tr>
<tr>
<td>FR</td>
<td>43 ± 2</td>
<td>735 ± 2</td>
<td>76 ± 2</td>
<td>63 ± 2</td>
<td>21 ± 8</td>
</tr>
<tr>
<td>IF</td>
<td>46 ± 7</td>
<td>858 ± 432</td>
<td>75 ± 1</td>
<td>65 ± 2</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>BK</td>
<td>45 ± 2</td>
<td>815 ± 15</td>
<td>75 ± 1</td>
<td>57 ± 4</td>
<td>21 ± 3</td>
</tr>
<tr>
<td>SM</td>
<td>47 ± 1</td>
<td>901 ± 93</td>
<td>75 ± 1</td>
<td>66 ± 3</td>
<td>19 ± 6</td>
</tr>
</tbody>
</table>

Values followed by different letters are significantly different (P = 0.05).

a FR, deep fried; IF, polyphosphate injected and fried; BK, baked; SM, smoked.

trout. The fat content, expressed on dry basis, remained fairly constant with cooking; they suggested that fat losses during cooking were offset by proportional or higher moisture losses during cooking. While loss of lipids containing pesticide would decrease residues in fish during cooking, the reduction of water content would tend to increase residue concentrations.

The organochlorine reductions observed in our study are higher than those observed by Armbruster et al. (4). They reported a reduction in PCB residues of 7.4% (db) in bluefish due to frying, baking, broiling, and poaching (internal temperature ranged from 75 to 90°C). They did not report significant differences due to the various cooking methods. In another study with striped bass, Armbruster et al. (3) found an overall reduction of about 13 to 15% (db) in PCB levels using six cooking methods (baked, broiled, fried, microwave, poached and steamed) and they found that the changes in PCB residues as a result of cooking method were not significantly different.

Residue reductions from four cooking methods were compared using Fisher's p-LSD difference of means test. FR, IF, and SK caused higher reduction in dieldrin concentration (db) when compared to BK. All of these methods resulted in significant reductions in dieldrin and DDE residues. In the case of DDE, SK- and IF-cooked fish fillets had greater reduction in DDE residues (db) than FR- or BK-cooked fish. Smoking produced the greatest reduction of DDE residues (on average 82%) among the four methods of cooking.

Residue reductions due to FR were 57 to 76% (db) for dieldrin and 47 to 58% (db) for DDE. Puffer et al. (8) found 39 to 74% (wb) losses in DDT and 28 to 65% (wb) for PCBs in pan-fried white croaker. The total losses in the present study for the FR fish were 46.4% (wb) with a range of 31 to 63% for dieldrin and 30.9% (wb) and a range of 20 to 37% for DDE, which are comparable to their findings. Changes in residue content following frying are in accordance with those obtained by Reinert et al. (9), who observed that frying and broiling reduced DDT by 64 to 72% (db) in Lake Michigan bloater.

IF cooking, in which fish fillets are injected with a polyphosphate solution, frozen, and then fried, is a widely used commercial method for processing catfish as it minimizes drip losses during cooking and prevents gaping (1, 6). Comparing residue levels for fish cooked by the two frying methods indicates that the two methods are not significantly different (P < 0.05) for reducing dieldrin, but IF fish had significantly less DDE than FR fish. In the case of IF fish, water is added by injecting a polyphosphate solution to an average weight gain of 10%. This may be a cause of variations in fat and moisture losses during cooking when comparing the two frying methods. Total moisture loss for FR-processed dieldrin-fed fish was 17.8% and fat increased by 35% (db), while in the case of IF-processed fish, moisture

TABLE 2. Residues in six raw and cooked fish fillets from p,p'-DDE-fed catfish prepared by frying, baking, or smoking or analyzed raw

<table>
<thead>
<tr>
<th>Parameter catfish fillet</th>
<th>Moisture (%)</th>
<th>Fat (%)</th>
<th>Wet basis</th>
<th>Dry basis</th>
<th>% fat basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>p,p'-DDE (ppb) mean ± SD (n = 6)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooking method</td>
<td>Length (cm)</td>
<td>Weight (g)</td>
<td>Raw</td>
<td>Cooked</td>
<td>Raw</td>
</tr>
<tr>
<td>FR</td>
<td>47 ± 1</td>
<td>904 ± 9</td>
<td>77 ± 1</td>
<td>65 ± 1</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>IF</td>
<td>45 ± 1</td>
<td>804 ± 161</td>
<td>77 ± 2</td>
<td>62 ± 2</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>BK</td>
<td>46 ± 2</td>
<td>820 ± 170</td>
<td>76 ± 2</td>
<td>61 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>SM</td>
<td>47 ± 1</td>
<td>956 ± 6</td>
<td>76 ± 1</td>
<td>64 ± 3</td>
<td>31 ± 8</td>
</tr>
</tbody>
</table>

Values followed by different letters are significantly different (P = 0.05).
loss was 12.5% and fat increased by 6.1% (db). For DDE-fed fish, fat was reduced by 17% (db) in FR cooked fish. The moisture contents for DDE-fed fish were reduced by 19.2% and 15.5% for IF- and FR-cooked fish, respectively.

Baking reduced both dieldrin and DDE by 48 to 50% (db). On a wet basis, 15.4% and 20.0% reductions were observed for dieldrin and DDE, respectively. The results obtained for dieldrin during baking compare well with a study by Skea et al. (10). They reported frying to be more effective than baking for reducing residues of Aroclor 1254, mirex, and DDE in smallmouth bass. Trotter et al. (13) reported that baking of bluefish resulted in a 27% decrease of PCBs which includes losses during skinning since raw fish were analyzed with skin on. This study also reports a loss of 15 to 25% (wb) for DDE during baking. Their results are comparable to the results of this study, where losses during baking were 20.0% (wb) for DDE and 15.4% for dieldrin.

Smoking is found to cause the greatest (82% db) reduction of DDE for the four cooking methods studied. Dieldrin was reduced by 61% during smoking. The result for DDE contradicts the findings of Reinert et al. (9), who found smoking to be less effective than frying and broiling. Our reductions of dieldrin during smoking compare well with those of Lewis et al. (7). They reported that average reduction of mirex in smoked brown trout from Lake Ontario of 35.7% (wb). The results of the current study suggest an overall reduction of 43.8% (wb) for dieldrin in smoked fish. In both cases, reductions in residues were found to be significant (P < 0.05). Skea et al. (10) significantly reduced levels of mirex, Aroclor 1254, and DDE by 38.7, 26.7, and 27%, respectively, in brown trout by smoking.

Numerous studies have suggested that losses of organochlorines during cooking can be attributed to the loss of fat (9, 10, 12, 16) and moisture (11, 14, 15). Puffer et al. (8) suggested that the influence of initial residue concentration was an important factor affecting the final concentration following cooking. Stachiw et al. (12) noted that the increase in surface area of the fish during cooking (patties from carp surimi) had a significant (P > 0.05) impact on the removal of tetrachlorodibenzo-p-dioxin (TCDD) in carp surimi during cooking. Also, increasing the end-point temperature of cooking was reported to significantly (P < 0.01) affect losses of TCDD. They also found that TCDD reductions were not significantly (P < 0.05) affected by the concentrations of TCDD in the raw sample, which is in contrast with the findings of Puffer et al. (8) who studied white croaker and found a 39 to 74% reduction in DDT. Puffer et al. (8) also found that reductions were higher for fish with greater initial residue concentrations. Zabik et al. (15) found negligible effects of cooking carp fillets on PCB's and other xenobiotics, and attributed it to the fact that carp is a lean fish (average fat 7.7 ± 3.2%), which may not render fat sufficient to cause significant losses of pesticides during cooking. They reported that fish with higher fat content may show significant pesticide losses during cooking and that leaner fish may lose less residues during processing. This is in contradiction with the findings of the current study where average fat content of raw catfish fillets was 5.3% for dieldrin-fed fish and 7.8% for DDE-fed fish and losses of organochlorines were as high as 80% for DDE. Skea et al. (10) investigated brown trout and attempted to correlate the loss of organochlorines during smoking to the amount of oil lost. They found that the percentage of oil lost was not significantly correlated with changes in concentrations of mirex or Aroclor 1254. Only DDE showed a significant correlation with lipid changes during processing. Wanderstock et al. (14) indicated that the reduction in DDT may be the result of oil lost as a result of cooking or by direct volatilization of the compound. Armbruster et al. (3) found losses of PCBs in drippings during baking to be insignificant and argued that losses due to volatilization may be more significant. They suggested that trimming of fillet may have increased the effects of processing by increasing the surface area and subsequent volatilization of residues.

It is evident from these findings that there is no certain factor which can explain the losses of organochlorines during cooking. Since most of the organochlorines are semivolatile and fish are subjected to high temperatures during cooking, losses due to volatilization may be more important than other factors. Therefore, an increase in surface area and cooking time would be expected to increase volatilization.

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REFERENCES


