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Tetrachlorodibenzo-*p*-dioxin Residue Reduction by Cooking/Processing of Fish Fillets Harvested from the Great Lakes

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Dioxins are ubiquitous environmental contaminants produced during some combustion processes, such as waste incineration, and are also the unwanted by-products of various chemical manufacturing and bleaching processes. Fehringer *et al* (1985) found fish collected in 1983 from Saginaw Bay and corresponding rivers to have the highest 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) levels with values ranging from nondetectable to 102 ppt. Fish from other Michigan rivers contained <10 ppt TCDD. EPA (1992) found TCDD in 70% of the samples analyzed for the national monitoring study with a mean level of 6.9 ppt and a median level of 1.38 ppt.

An early study (Kaczmar 1983) showed that charbroiling three carp fillets resulted in extremely variable but substantial loss of 30 to 70% TCDD. Stachiw *et al* (1988) found losses of 40 to 70% during roasting or charbroiling restructured carp fillets prepared using carp surimi. The percentage loss was approximately the same for fillets which were spiked to 100 ppt in the raw surimi as compared the the fillets from surimi with about 50 ppt. Increasing the end internal temperature from 60 to 80°C or increasing the surface area increased the loss.

As part of a larger study to determine to amount of contamination of Great Lakes fish at the dinner table, composite raw and cooked samples were analyzed for TCDD. Five fish species were studied from all of the Great Lakes.

MATERIALS AND METHODS

Harvesting, processing and cooking data for skin-on and skin-off carp (*Cyprinus carpio*) from Lakes Huron and Erie and skin-on and skin-off chinook salmon

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(Oncorhynchus tshawytscha) from Lakes Huron and Michigan are given in Zabik *et al* 1995b, for skin-off lake trout (*Salvelinus namaycush*)[lean and fat (siscowets)] from Lakes Huron, Michigan, Ontario and Superior in Zabik *et al* 1995c and for skin-on walleye (*Stizo-tedium vitreum vitreum*) from Lakes Erie, Huron and Michigan and skin-on white bass (*Morone chrysops*) from Lakes Erie and Huron in Zabik *et al* 1995a. Fish size was chosen to represent mean sizes caught by sports fishermen. Carp were pan and deep fat fried. Chinook salmon were baked, charbroiled, scored and charbroiled and canned. Lake trout were baked and charbroiled from all lakes and lake trout from Lake Michigan and siscowets from Lake Superior were also salt boiled and smoked. Walleye from all lakes were baked and charbroiled and Lake Michigan walleye were also deep fat fried. White bass were pan fried. Six fish fillets were prepared for each cooking methods. Due to the complexity of the analyses and the cost, all six raw fish and all six cooked fish from one species prepared by one method from one lake were composited and the level in the composite raw and cooked sample compared to determine the reduction due to cooking.

TCDD analyses were carried out following the procedure outlined in Stachiw *et al* (1988). Reversed-phase HPLC sample clean-up was followed by GC/MS quantitation. The concentration of 2,3,7,8-TCDD present in the composite fish sample was calculated by

$$\text{ppt (ng/kg) } 2,3,7,8\text{-TCDD} = \frac{AE}{CH}\,\frac{DG}{BF}$$

where A = peak area of native 2,3,7,8-TCDD in the composite sample, B = peak area of added (^{13}C)-2,3,7,8-TCDD in the sample, C = peak area of (^{12}C)-2,3,7,8-TCDD in the standard, D = peak area of (^{13}C)-2,3,7,8-TCDD in the standard, E = weight of (^{12}C)-2,3,7,8-TCDD in the standard (ng), F = weight of (^{13}C)-2,3,7,8-TCDD in the standard (ng), G = weight of (^{13}C)-2,3,7,8-TCDD added to the sample (5 ng) and H = weight of composite fish sample (kg). Percentage recovery and the limit of detection was calculated for each composite sample analyzed and ranged from 75 to 94% with a mean of 86$\pm$2.5% and 0.1 to 0.5 pptr with a mean of 0.1$\pm$0.1 pptr, respectively. The ppt and the weight of the raw and cooked fish fillets composites were used to calculated picograms per six fish to calculate the percent loss.

RESULTS AND DISCUSSION

The levels of TCDD in the composite samples of

siscowets from Lake Superior were below the limit of detection. Of the composites which had detectable levels, white bass had the lowest levels of TCDD with 0.6 ppt in the composite from Lake Huron and 0.5 ppt in the composite from Lake Erie. Lake trout and chinook salmon all had residue levels in the composites below 10 ppt TCDD. The levels of TCDD in the raw lake trout were as follows: 4.3 ppt for Lake Huron, 4.0 ppt for Lake Michigan and 3.3 ppt for Lake Ontario. For Lake Michigan, raw skin-on chinook salmon had 7.83 ppt and raw skin-off had 7.6 ppt while for Lake Huron, raw skin-on lake trout had 4.53 ppt and raw skin-off had 3.75 ppt. The similarity of residue levels in the skin-on and skin-off fillets shows that TCDD is fairly ubiquitiously distribulted in the fish tissue.

Residue levels in raw carp and walleye differed considerably by the lake from which the fish were harvested. Raw skin-on walleye fillets harvested from Lake Michigan had 2.2 ppt TCDD while walleye harvested from Lake Erie had 13.5 ppt and from Lake Huron, 10.5 ppt. Industrialization of the region could account for these differences as the walleye from Lake Michigan were harvested from Little Bay de Noc in the Upper Penisula of Michigan and those from Lakes Erie and Huron from waters off Monroe, MI and from Saginaw Bay, respectively.

Although the carp and walleye had both been harvested from similar locations in Lakes Huron and Erie, the Lake Huron carp had more than four times the residues of TCDD than did those from Lake Erie. Values for TCDD residues in the walleye from the two lakes had been much closer in values. Skin-on carp from Lake Huron had 22.6 ppt of TCDD while skin-on carp from Lake Erie had 5.4 ppt. A similar relationship occurred for the skin-off carp fillets, carp from Lake Huron had 23.1 ppt TCDD and those from Lake Erie had 5.3 ppt. The fact that the carp from Saginaw Bay in Lake Huron had twice the TCDD than the walleye harvested from a similar location relates to the feeding patterns of these fish. Carp are bottom feeders while walleye are gamefish. Age was not a factor since the carp were 3.2 ± 1.3 years and the walleye were 4.1 ± 1.2 years. EPA (1992) reported carp had seven times the level of TCDD as walleye but they analyzed the carp as whole body samples and the walleye as fillets.

For both the chinook salmon and carp, skin-on and skin-off raw fillets had very similar levels of TCDD. Trimming had previously been shown to effectively reduce the levels of pesticides and total PCBs in raw

fish fillets (Hora 1981, Sanders and Haynes 1988, Zabik *et al* 1995b). Zabik *et al* 1995b reported that trimming the lateral line and associated fat significantly reduced the fat level in the processed fillet and correlated this loss of fat to the lower level of pesticides and total PCBs in the skin-off chinook salmon and carp fillets than in the skin-on fillets. TCDD seems less associated with the fat since trimming the lateral line and associated fat did not reduce the levels of TCDD in these skin-on fillets.

TCDD residues were lower in all cooked composites than in the corresponding raw samples. Total picrograms in the cooked composite was compared to that in the raw composite to evaluate the percent reduction. The reduction in TCDD by each of the seven cooking methods used in this study is shown in Figure 1. Smoking reduced residue levels of TCDD found in the Lake Michigan lake trout. Smoking has been shown to be the most effective process to reduce pesticides and total PCBs from lake trout but residues of polynuclear aromatic compounds that are formed during smoking are increased (Zabik *et al* 1995c). Salt boiling was the least effective cooking method for the reduction of TCDD and this was also true for reducing pesticides and total PCBs (Zabik *et al* 1995c). Canning resulted in a loss of 34% TCDD while the other cooking methods resulted in losses of about 50%. Loss of TCDD during cooking and processing were generally greater than the percentage reductions found for pesticides and total PCBs which averaged 33% (Zabik *et al* 1995a, Zabik *et al* 1995b, Zabik *et al* 1995c). These losses also were in the range of those found in the two earlier studies (Kaczmar 1983, Stachiw *et al* 1988).

Average losses of TCDD for the five species of Great Lakes fish is presented in Figure 2. The greatest percentage loss was 80% for the white bass. Other species which were processed as skin-on fillets had lower losses of about 40% TCDD than the species which were processed as skin-off fillets. Skin-off carp lost an average of 54% TCDD while skin-on carp had 36% TCDD losses. Skin-off chinook salmon lost an average of 57% TCDD and skin-on chinook salmon lost an average of 43% TCDD. Therefore, it can be recommended that these fish be processed skin-off to enhance TCDD losses. This form of processing will also reduce the level of other halogenated xenobiotics in the cooked fish fillets (Hora 1981, Sanders and Haynes 1988, Zabik *et al* 1995b).

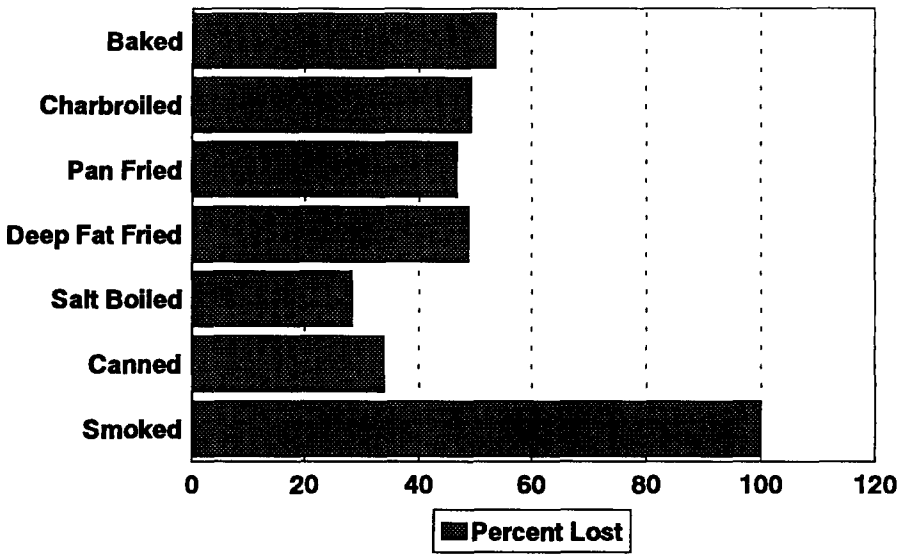

Figure 1. Effect of cooking/processing methods on TCDD reduction from Great Lakes fish.

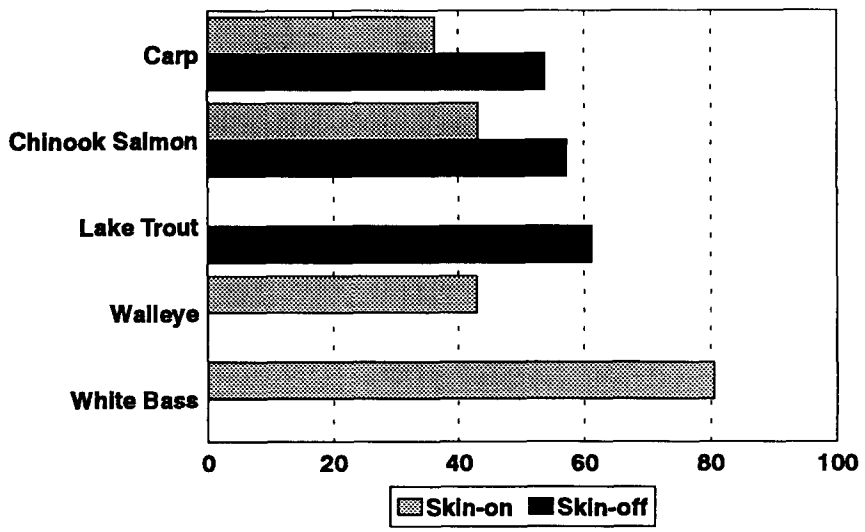

Figure 2. TCDD reduction during cooking and processing of five species of Great Lakes fish.

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