

Pesticides and Total Polychlorinated Biphenyls Residues in Raw and Cooked Walleye and White Bass Harvested from the Great Lakes

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To provide data for public health and other government officials to quantitate the degree of exposure a human might receive from consumption of commonly sought open water fish species prepared and cooked by commonly used methods, five species of Great Lakes fish were chosen. Data is presented for walleye harvested from Lakes Erie, Huron and Michigan which were baked and char-broiled as skin-on fillets with additional walleye from Lake Michigan being deep fat fried. Skin-on white bass fillets from Lakes Erie and Huron also were pan fried.

Packed column PCB and pesticide analyses were conducted for all fish species by the Michigan Department of Public Health. The DDT complex (*p,p'*DDT, *p,p'*DDE and *p,p'*DDD), dieldrin, hexa-chlorobenzene (HCB), chlorodane complex (alpha and gamma chlordanes, oxychlordanes, *cis*- and *trans*-nonachlor), toxaphene, heptachlor epoxide, and total PCBs (expressed as Arochlor[®] 1254) were found at above the minimum level of detection for many of the species studied. Residues were expressed as ppm wet tissue and then converted to micrograms per fillet to calculate the percentage loss due to cooking.

MATERIALS AND METHODS

White bass (*Morone chrysops*) and walleye (*Stizostedion vitreum vitreum*) were chosen to be representative of the mean Creel census data from sports fisherman for 1990. Walleye and white bass were caught in Lake Erie on April 22, 1991 at 41°51.5N, 83°20.1W. Walleye were caught in Lake Michigan on April 12, 1991 at the north end of Little Bay de Noc. White bass and walleye were caught in Lake Huron in Saginaw Bay on July 22 and 25, 1991, respectively. Walleyes from Lake Erie averaged 5.0±1.3 yr while Lake

Huron walleye averaged 4.1 ± 1.2 yr. Walleye from Lake Michigan were 4.1 ± 0.7 yr. All the walleye were male. Lake Erie white bass averaged 2.8 ± 0.8 yr while Lake Huron white bass were 2.7 ± 0.7 yr. All of the Lake Erie white bass were male, while all of the Lake Huron white bass were female.

Fish were processed at the Michigan State University Meats Lab within one day of catch according to recommendations for sports fishermen so skin-on fillets had the belly flap removed. Six fish from each lake were prepared by each cooking method. From these three raw and cooked sets were selected at random for pesticide and total PCB analyses. Individual congeners of PCBs were determined for all six fish and will be reported elsewhere. Baking and charbroiling was carried out as described by Stachiw et al (1988). Fish were deep fat fried as outlined in Morehouse and Zabik (1989). Fish fillets were pan fried according to the procedure of Puffer and Gossett (1983). Cooked samples contained only muscle tissue for all cooking methods except deep fat frying. Deep fat fried skin-on fillets included the skin as well as the muscle tissue since deep fat fried fish usually have either breading or a batter and would be eaten only with the skin.

Pesticides and total PCBs were determined using extraction and cleanup methods as well as packed column electron capture gas chromatographic analyses as outlined by Price et al (1986). Percentage fat was determined as part of these analyses. The following gives the levels of detection: *p,p'*-DDT, 0.005 ppm; *p,p'*-DDE, 0.003 ppm; *p,p'*-DDD, 0.005 ppm; α -Chlordane, 0.003 ppm; γ -Chlordane, 0.003 ppm; Oxychlordane, 0.003 ppm; *cis*-Nonachlor, 0.003 ppm; *trans*-Nonachlor, 0.003 ppm; HCB, 0.001 ppm; Dieldrin, 0.005 ppm; Heptachlor epoxide, 0.003 ppm; Toxaphene, 0.050 ppm; Total PCBs, 0.025 ppm. Ten percent of the samples were run in duplicate. Variability of the pesticide and total PCB analyses was: *p,p'*-DDT, $11.8 \pm 12.0\%$; *p,p'*-DDE, $7.8 \pm 10.5\%$; *p,p'*-DDD, $6.8 \pm 6.5\%$; α -Chlordane, $10.5 \pm 9.6\%$; γ -Chlordane, $13.6 \pm 16.9\%$; Oxychlordane, $5.5 \pm 9.3\%$; *cis*-Nonachlor, $4.5 \pm 5.3\%$; *trans*-Nonachlor, $14.4 \pm 16.8\%$; HCB, $4.3 \pm 8.7\%$; Dieldrin, $4.6 \pm 6.5\%$; Heptachlor epoxide, $21.8 \pm 49.8\%$; Toxaphene, $6.5 \pm 6.7\%$; Total PCBs, $6.6 \pm 11.3\%$.

RESULTS AND DISCUSSION

p,p'-DDE was the primary component of the DDT complex accounting for over 80% of the values in Table 1. *p,p'*-DDD was generally found at higher levels than *p,p'*-DDT with *p,p'*-DDT being below the limit of detection in some of the walleye from Lakes Erie and

Table 1. Levels of pesticides and polychlorinated biphenyls (PCBs) in raw skin-on¹ walleye and white bass from the Great Lakes.

Fish	Environmental	Lake		
Species	Contaminants	Erie ²	Huron ²	Michigan ³
		ppm in wet tissue		
Walleye	Chlordane			
	Complex	0.030	0.034	0.022
	DDT Complex	0.078	0.083	0.079
	Dieldrin	0.009	0.008	0.006
	Toxaphene	ND	0.09	0.05
	Total PCBs	0.42	0.24	0.20
White Bass	Chlordane			
	Complex	0.047	0.034	
	DDT Complex	0.139	0.110	
	Dieldrin	0.011	0.011	
	Toxaphene	ND	0.08	
	Total PCBs	0.76	0.50	

¹Belly flap removed.

²n=6 for walleye; n=3 for white bass.

³n=9 for walleye.

ND is below the minimum detectable level.

Huron. *trans*-Nonachlor, followed by *cis*-nonachlor, were the major components of the chlordane complex even though these compounds were minor components of technical chlordane. HCB, heptachlor epoxide and toxaphene were found only in a few of the walleye fillets. HCB and heptachlor epoxide were always below the level of detection for Lake Michigan walleye but occurrence of these three pesticides were scattered in the walleye fillets from the other two lakes.

Residues in the raw walleye from Lakes Erie, Huron and Michigan were the lowest of any of the five species studied and did not differ by lake except that the total PCBs in the Lake Erie walleye were about twice the PCBs in those from Lakes Huron or Michigan (Table 1). This difference is not related to size or percentage fat. Walleye from Lake Huron were longer and heavier (48.6 cm; 1064 g) than those from Lakes Erie and Michigan (46.1 cm, 897 g; 46.4 cm, 770 g, respectively). In addition walleye from Lake Erie were heavier than those from Lake Michigan. Percentage fat was 1.7%, 3.0% and 1.1% in raw walleye from Lakes Erie, Huron, and Michigan, respectively. Carcass yield of

walleye from Lakes Erie (66.5%) and Michigan (63.4%) were higher than that of walleye from Lake Huron (59.7%). Thus, walleye from Lake Huron were trimmed more to remove the visible belly flap fat even though they still were slightly higher in fat. Location of catch appears to be the determinant of PCB level but not for pesticide residues.

Residues in raw white bass are also given in Table 1. Again the white bass from Lake Erie had higher levels of PCBs than those from Lake Huron. White bass and walleye from Lake Erie were harvested from the same location on the same day. White bass from Lakes Erie and Huron were the same length (31 cm) but Lake Erie white bass weighed close to twice (677 g) that of Lake Huron white bass (382 g). Fat content of the Lake Erie white bass was 4.4% as compared to 2.6% for Lake Huron white bass. White bass harvested from Lake Huron had significantly higher (64.5%) carcass yield than those from Lake Erie (59.5%).

Baking, charbroiling and deep fat frying walleye resulted in an average cooking loss of 22.5%, 24.1% and 36.7%, respectively. To account for the differences in the weights of the raw and cooked samples the ppm wet tissue was converted to micrograms per fillet. These values are presented in Table 2 for the total PCBs and pesticides consistently found in the walleye samples. The cooked deep fat fried walleye fillets contained the skin while the other cooked samples contained the muscle tissue only. The micrograms of the chlordane and DDT complexes in the cooked deep fat fried walleye were almost the same as that in the raw but the standard deviations of these data were high. Although the skin was finally cut before being homogenized with the muscle tissue, perhaps more sample deviation occurred. Loss of dieldrin from the deep fat fried fish was 26.4% which compares well to the average loss of 23.1% for all cooking methods. Losses of pesticides and PCBs were close to or greater than the cooking losses for most of the baked or charbroiled walleye. Average losses ranged from 18.3% for DDT complex and total PCBs to 23.6% for the chlordane complex and were about 10% less than had been found for cooking chinook salmon or carp (Zabik et al 1994) but the latter two species had much higher levels of residues in the raw fish.

The micrograms of pesticides and total PCBs in the white bass are presented in Table 3. Pan frying the white bass resulted in losses of 17 to 53%. The greatest variation was for dieldrin which occurred at the lowest levels. Pan fried Lake Erie white bass lost 17% dieldrin while pan fried Lake Huron white bass lost

Table 2. Pesticides and total polychlorinated biphenyls (PCBs) expressed as micrograms raw, baked, charbroiled or deep fat fried walleye fillet¹ from Lakes Erie, Huron and Michigan.

Compounds	Baked ²		Charbroiled ²		Deep Fat Fried ³	
	Raw	Cooked	Raw	Cooked	Raw	Cooked
Lake Erie						
Chlordane						
Complex	1.00	0.67	3.42	1.38		
DDT Complex	4.28	2.85	9.12	6.85		
Dieldrin	0.47	0.37	1.03	0.73		
Total PCBs	19.63	17.00	54.95	44.08		
Lake Huron						
Chlordane						
Complex	2.27	1.27	2.39	1.80		
DDT Complex	8.40	6.18	6.45	5.33		
Dieldrin	1.05	0.95	1.03	0.65		
Total PCBs	35.56	28.43	19.92	14.18		
Lake Michigan						
Chlordane						
Complex	2.09	1.90	1.00	0.67	2.20	2.14
DDT Complex	8.24	6.43	4.28	2.85	7.96	7.74
Dieldrin	0.69	0.51	0.68	0.60	0.52	0.38
Total PCBs	18.70	14.33	21.40	15.63	20.38	17.41

n=3

¹Skin-on fillet has belly flap removed.

²Cooked sample contained muscle tissue only.

³Cooked sample contained skin and muscle tissue.

53% of its dieldrin. Average losses for pan frying white bass were 37.5% for the chlordane complex; 35.8% for the DDT complex; 34.8% for dieldrin; and 28.3% for total PCBs. These percentages are slightly higher than those for the walleye.

Some early studies showed inconsistent or minimal losses of pesticides and PCBs (Cin and Kroger 1982 -- mirex in brown trout; Smith *et al* 1973 -- PCBs and DDT in chinook and coho salmon; Zabik *et al* 1982 -- PCBs, DDD and DDE in carp). Most of the authors suggested the low fat content of the fish used in these studies may have accounted for the minimal loss. Broiling fat lake trout (siscowets) reduced PCBs, DDT compounds and dieldrin by 39 to 53% while roasting or cooking by microwave resulted in more varied losses ranging from 25 to 54% (Zabik *et al* 1979).

A companion study evaluated the losses of

Table 3. Pesticides and PCBs expresses as micrograms per raw¹ and pan fried² white bass.

Compound	Lake Erie		Lake Huron	
	Raw	Fried	Raw	Fried
Chlordane				
Complex	3.60	2.17	0.95	0.62
DDT Complex	10.98	7.44	5.17	3.23
Dieldrin	1.55	1.28	0.56	0.26
Total PCBs	57.22	46.70	28.29	15.75

n=3.

¹Skin-on fillet; belly flap removed.

²Cooked sample contained muscle tissue only.

pesticides and total PCBs during the baking, charbroiling or canning of chinook salmon from Lakes Huron and Michigan and during the pan frying or deep fat frying of carp from Lakes Erie and Huron (Zabik et al 1994). Average losses of pesticides and total PCBs from chinook salmon ranged from 30 to 41%. The loss from the DDT complex was 30% while the loss of all the other compounds was greater than 35% and the average loss of HCB, heptachlor epoxide and total PCBs were all 41%. Similar average percentage losses were found for carp ranging from 30 to 35% for the DDT complex, chlordane complex and total PCBs while the losses of HCB and dieldrin were greater than 40%. Location did not affect the percentages lost. In contrast, Puffer and Gossett (1983) reported substantial differences in the reduction of DDT and PCBs during pan-frying croaker fillets based on location from which the fish were caught (74 and 65%, respectively vs 39 and 28%). Nevertheless, the minimum losses found by Puffer and Gossett were in the range of the current study.

The current study showed the level of pesticides and PCBs in walleye and white bass of a size representing the mean size caught by sports fisherman to be low and that cooking reduces the level of these contaminants by another 1/4 to 1/3. Significant differences ($p > 0.05$) were not seen among the cooking methods used except including the skin on the deep fat fried walleye minimized the loss of the chlordane and DDT complexes. Deep fat fried skin-on carp fillets which also had the skin included in the cooked samples also had lower losses than did pan fried skin-on carp fillets which had only the muscle tissue in the cooked

sample (Zabik et al 1994). Therefore cooking methods that allow the separation of the cooked muscle from the skin reduce the amount of contaminants the consumer would ingest.

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REFERENCES

- Cin DA Kroger M (1982) Effects of various kitchen heat treatments, ultraviolet light and gamma irradiation on mirex insecticide residues in fish. J Food Sci 47:350-352
- Morehouse SE Zabik ME (1989) Evaluation of polydimethylsiloxane fluids as non-caloric frying media. J Food Sci 54:1061-1065
- Price HA Welch RL Scheel RH Warren LA (1986) Modified multiresidue method for chlordane, toxaphene, and polychlorinated biphenyls in fish. Bull Environ Contam Toxicol 39:1-9
- Puffer HW Gossett RW (1983) PCB, DDT, and benzo(a)pyrene in raw and pan-fried white crocker (*Genyonemus lineatus*). Bull Environ Contam Toxicol 30:65-73
- Smith WE Funk K Zabik ME (1973) Effects of cooking on concentrations of PCB and DDT compounds in chinook (*Oncorhynchus tshawytscha*) and coho (*O. kisutch*) salmon from Lake Michigan. J Fish Res Board Can 30:702-706
- Stachiw NC Zabik ME Booren A Zabik MJ (1988) Tetrachlorodibenzo-p-dioxin residue reduction through cooking/processing of restructured carp fillets. J Agric Food Chem 36:848-853
- Zabik ME Hoojjat P Weaver CM (1979) Polychlorinated biphenyls, dieldrin and DDT in lake trout cooked by broiling, roasting or microwave. Bull Environ Contam Toxicol 21:136-143
- Zabik ME Merrill C Zabik MJ (1982) PCBs and other xenobiotics in raw and cooked carp. Bull Environ Contam Toxicol 28:710-715
- Zabik ME Zabik MJ Booren AM Nettles M Song J-H Welch R Humphrey H (1995) Pesticides and total polychlorinated biphenyls in chinook salmon and carp harvested from the Great Lakes: Effects of skin-on and skin-off processing and selected cooking methods. J Agric Food Chem 43:In press