

# Pesticide residues, PCBs and PAHs in baked, charbroiled, salt boiled and smoked Great Lakes lake trout

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Skin-off lean lake trout (Salvelinus namaycush namaycush) from Lakes Huron, Michigan and Ontario as well as siscowets (fat lake trout) (Salvelinus namaycush siscowet) from Lake Superior were cooked by baking and charbroiling to determine the potential of processing/cooking on reducing the levels of pesticides and total PCBs in fish at the dinner table. Lake trout from Lakes Michigan and Superior also were salt boiled and skin-on fillets smoked. All fish analyzed were below the action level except skin-on siscowets with > 0.3 ppm action level for chlordane. Cooked lake trout had significantly less residue than raw. Smoking resulted in significantly greater losses of pesticides and total PCBs than other cooking methods but analyses of polynuclear aromatic hydrocarbons showed significant compound formation during smoking with higher levels occurring in high fat siscowets. Overall losses of pesticides and total PCBs ranged from a low of 21% for dieldrin to a high of 39% for chlordane complex. Most of the total losses were about 30% establishing that cooking is effective in reducing residues in these Great Lakes fish.

# INTRODUCTION

Fish are an excellent source of protein and omega fatty acids yet the fear of contaminant levels influences the use of this Great Lakes resource. To maximize the use of this resource, it is essential to know the level of contaminants in processed/cooked fish as eaten by sports fishermen and their families at the dinner table. Tourism, charter boat fishing industry and Native American fisheries are all adversely affected by consumers' fear of contaminants in Great Lakes fish. Risk assessment should consider residue levels as eaten. Several studies have shown some reduction of pesticides and PCBs during processing and cooking of fish (Zabik *et al.*, 1979; Armbruster *et al.*, 1989; Sanders & Hayes, 1988).

A recent Environmental Protection Agency (1992) national study of chemical residues in fish showed that more than half the sites had fish with detectable levels of p,p'-DDE, biphenyl, mercury, total PCBs, *trans*-nonachlor, pentachloroanisole, *cis*- and *trans*-

chlordane, dieldrin,  $\alpha$ -BHC and 1,2,4 trichlorobenzene. Whole bottom-feeding fish such as carp and game fish fillets such as white bass harvested at the same locations were analyzed in this EPA national study. While only a few of the sites were in the Great Lakes, many fish with the highest level of contamination were from sites in the Great Lakes basin.

In order to assess the potential reduction of environmental contaminants from several species of Great Lakes fish using sizes and locations for harvesting fish common to those of typical sports fisherman, a comprehensive study was conducted to assess the level of contaminant consumption at the dinner table. This paper will present data related to the effect of processing and cooking on the levels of organochlorine pesticides and total PCBs in skin-off lean lake trout (Salvelinus namaycush namaycush) harvested from Lakes Huron, Michigan and Ontario and siscowets (fat lake trout) Salvelinus namaycush siscowet) from Lake Superior. Lake trout and siscowets from these Great Lakes were cooked by baking and charbroiling. In addition, lake trout and siscowets from Lakes Michigan and Superior were salt boiled and smoked. Since smoking meats is known to contribute to the formation of polynuclear

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aromatic hydrocarbons (PAHs), the smoked lake trout from Lake Michigan and the siscowets from Lake Superior were also analyzed for PAHs.

# MATERIALS AND METHODS

#### Fish

Lake trout (lean) from Lakes Huron, Michigan and Ontario was chosen to represent the mean Creel census data from sports fisherman for 1990 (Rakoczy, 1991). Size of siscowets was selected based on averages of catch from Native American fisheries. Lake trout were caught in Lake Huron at South Point in 36-80 feet of water on 4 June 1991. Lake trout were caught in Lake Michigan from 17-19 April 1991 to 14-15 May 1991 at Pentwater, grids 1409 and 1509. Lake trout from Lake Ontario were caught at Cape Vincent on 4 September 1991. Siscowets were caught in Lake Superior at Marquette, Michigan (46°41.61N, 87°19.21W) on 19 June 1991.

Lake trout from Lake Huron had mean age, weight and lengths of  $6.2 \pm 0.4$  years,  $2.7 \pm 0.4$  kg and  $63.7 \pm 3.1$  cm. Half the sample was male and half female. Lake trout from Lake Michigan averaged  $6.5 \pm 0.8$  years,  $2.7 \pm 0.7$  kg and  $63.7 \pm 5.5$  cm. Eighty-one percent of the Lake Michigan lake trout were female. Lake Ontario lake trout were  $5.3 \pm 0.5$  years,  $2.8 \pm 0.2$  kg and  $64.7 \pm 1.3$  cm. Siscowets from Lake Superior averaged  $9.2 \pm 0.9$  years,  $1.3 \pm 0.1$ kg and  $52.7 \pm 1.8$  cm; 71% of the siscowets were male.

# Fish processing/cooking

Fish were processed at the Michigan State University Meat Laboratory within 1 day of catch according to recommendations for sports fisherman so these skin-off fillets had the belly flap, skin, lateral line and associated fat removed. Six fish from each lake were portioned, wrapped in aluminum foil and vaccum packaged until subsequent analyses by each cooking method used. From these six pairs of raw and cooked lake trout fillets, three sets of raw and cooked fillets 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 of lake trout from all four lakes were carried out as described by Stachiw et al. (1988). Procedures in the Great Lakes Fish Preparation were used for salt boiling lake trout and siscowets from Lakes Michigan and Superior, respectively. All fish were cooked to an internal temperature of 80°C. Lake trout fillets from Lake Michigan and siscowets from Lake Superior were smoked as outlined by Bratzler and Robinson (1967). The final step in this process held the internal temperature of the fish at 82°C for 30 min.

#### Quantitation of pesticides and total PCBS

Pesticides and total PCBs were determined using extraction and clean-up methods, as well as packed

column electron capture gas chromatographic analyses, as outlined by Price et al. (1986). Percent 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;  $\alpha$ -chlordane, 0.003 ppm;  $\delta$ -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 ± 12.0%; p,p'-DDE, 7.8 ± 10.5%; p,p'-DDD,6.8±6.5%;  $\alpha$ -chlordane, 10.5±9.6%;  $\delta$ chlordane,  $13.6 \pm 16.9\%$ ; oxychlordane,  $5.5 \pm 9.3\%$ ; cisnonachlor,  $4.5 \pm 5.3\%$ ; 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±11.3%.

#### **Quantitation of PAHS**

All six samples of raw lake trout and siscowets and their corresponding smoked samples were analyzed for PAHs using EPA methods (Environmental Protection Agency, 1986). PAHs analyzed for included naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, benzo(b)fluoranthene, pyrene, benzo(a)fluorene, benzo(b)fluorene, 3,6-dimethylphenanthrene, benz(a)anthracene, perylene, benzo(a)pyrene, benzo(b)pyrene, dibenz(ac)anthracene, dibenz-(ah)anthracene, picene, indenol(1,2,3-cd)pyrene, anthanthene, dibenzo(ae)pyrene, 9,10-diphenylanthracene, dibenzo(ai)pyrene, dibenzo(ah)pyrene, chrysene and dibenzo(al)pyrene. Limits of detection for these compounds was 0.05 ppb.

#### Statistical analysis

Data were analyzed for variance using a general linear model with SAS (SAS Institute, Inc., Cary, North Carolina). Tukey's test was used to sort out significant differences of individual means at P < 0.05.

# **RESULTS AND DISCUSSION**

# Pesticides and total PCBS

p,p'-DDE was the primary component of the DDT complex accounting for over 80% of the values in Table 1. All values were about 10% or less of the 'action level' of 5 ppm and were lowest for the Lake Huron lake trout. *trans*-Nonachlor, followed by *cis*-nonachlor, were the major components of the chlordane complex even though these compounds were only minor components of technical chlordane. The residue level of the chlordane complex in the skin-on siscowets from Lake Superior exceeded the action level of 0.3 ppm. This was the only instance that any of the trout or siscowet fillets exceeded action levels. These siscowets were on average

Environmental contaminants	Skin on or off	Lake					
		Huron	Michigan	Ontario	Superior (siscowets)		
<u></u>		ppm					
Chlordane complex	On Off	0.098	0.190 0.128	0.114	0.308 0.258		
DDT complex	On Off	0.21	0.49 0.49	0.41	0.60 0.51		
Dieldrin	On Off	0.029	0.080 0.076	0.027	0.081 0.031		
НСВ	On Off	0.004	0.005 0.004	0.010	0.014 0.006		
Heptachlor epoxide	On Off	0.006	0.022 0.013	0.005	0.018 0.018		
Toxaphene	On Off	0.30	0.35 0.31	0.10	3.8 2.5		
Total PCBs	On Off	0.39	0.82 0.78	0.82	1.03 0.89		

Table 1. Levels of pesticides and polychlorinated biphenyls (PCBs) in raw skin-on<sup>a</sup> and skin-off<sup>b</sup> lake trout and siscowets from the Great Lakes

Skin-on samples n = 3; skin-off samples n = 6 for Lakes Huron and Ontario, n = 9 for Lakes Michigan and Superior.

<sup>a</sup>Belly flap removed.

<sup>b</sup>Belly flap, lateral line and associated fat removed.

3-4 years older than the other fish although they weighed half the amount of the lake trout. The skin-on siscowets had at least twice the percentage of fat (22.7%) of the skin-off siscowets or any of the lake trout (6.2-11.5%). The as-prepared yield of the skin-off siscowets was more than 5% less than that of the other skin-off lake trout fillets (i.e. 27.3% for skin-off siscowets and 31.8-33.3% for skin-off lake trout) showing greater trimming of the siscowets did reduce the fat in the remaining muscle tissue.

Dieldrin levels were higher in both Lake Michigan lake trout and Lake Superior siscowets but all were less than one-quarter of the action level of 0.3 ppm (Table 1). Toxaphene levels were highest for the Lake Superior siscowets but still below the action level of 5 ppm. Total PCBs were all below half of the action level of 2 ppm and were lowest for Lake Huron lake trout. Very low levels of HCB and heptachlor epoxide were found in the lake trout and siscowets.

Micrograms per fillet were calculated to compare the difference in the level of residues in the cooked fillets as compared to that in the raw fillet before cooking. The micrograms per fillet for the lake trout and siscowets from Lakes Huron, Michigan, Ontario and Superior that were baked or charbroiled are summarized in Table 2. Total cooking losses were highest for siscowets (26.0 and 25.2% for baking and charbroiling, respectively) and lowest for lake trout from Lake Ontario (17.3 vs 19.9%). Micrograms reflect both the level of residue and the size of the fish fillet.

The micrograms in the cooked fillets were less than that in the raw fillets but baking and charbroiling were equally effective in reducing these residues. None of the chlordane complex was found in the cooked fillets from lake trout harvested from Lake Ontario. Toxaphene was also below the limits of detection for charbroiled lake trout from Lake Ontario. Baking and charbroiling resulted in modest residue losses of 12–20% for DDT complex, HCB, dieldrin and total PCBs. Highest residue losses were found for the chlordane complex ranging from 35 to 38%.

For lake trout from Lake Michigan and siscowets from Lake Superior, the effect of salt boiling and smoking was compared to the reduction in pesticides and total PCBs from baking and charbroiling. The micrograms of pesticides and total PCBs in the raw and cooked lake trout from Lake Michigan and siscowets from Lake Superior is presented in Table 3. Again the micrograms in the cooked fillets were less than that in the raw fillets and smoking resulted in significantly greater reductions (P < 0.05) of the pesticides and total PCBs than any other method (Fig. 1).

Smoking reduced the pesticides and total PCBs by 40 to over 50%. This could be influenced by the long, slow processing followed by holding at a higher end temperature that resulted in significantly higher cooking losses of 40% as compared to cooking losses of approximately 30% for the other cooking methods. Visual observation during smoking indicated much of this additional loss was fat. Smoked lake trout and siscowets were also processed skin-on and only the muscle of the cooked sample was analyzed for pesticides and total PCBs. Nevertheless, comparisons of the percentage reductions during baking and charbroiling chinook salmon were similar for both skin-on and skin-off fillets (Zabik *et al.*, 1995*a*).

The average losses of pesticides and total PCBs are shown in Fig. 2. These average losses were generally

 Table 2. Pesticides and total polychlorinated biphenyls (PCBs) expressed as micrograms per raw and baked or charbroiled Lake Trout fillet harvested from Lakes Huron, Michigan, Ontario and Superior

	Bak	red	Charbroiled			
Compounds	Raw	Cooked	Raw	Cooked		
	Lake Huron (lean trout)					
<i>p.p</i> ′-DDT	594 + 3.14	4 92 + 2 51	$554 \pm 135$	363+0.04		
<i>p.p</i> ′-DDE	$36.7 \pm 12.2$	$30.2 \pm 2.51$	366+65	31 3 4 0 5		
$p_n p' - DDD$	304 + 154	$286 \pm 147$	$300 \pm 7.22$	33.3 ± 3.3 3 26 ± 3 20		
$\alpha$ -Chlordane	$3.04 \pm 1.04$ $3.79 \pm 1.99$	$2.00 \pm 1.47$ 3 54 + 2 04	$3.77 \pm 2.23$ $3.70 \pm 0.47$	$3.30 \pm 2.20$		
α-Chlordane	$759 \pm 1.12$	$1.31 \pm 0.86$	$3.70 \pm 0.47$	$3.03 \pm 0.41$		
Oxychlordane	$1.42 \pm 0.42$	$1.31 \pm 0.30$ 1 34 ± 0.52	$1.31 \pm 0.31$ 1.79 $\pm 0.94$	1.57		
cis-Nonachlor	$4.06 \pm 1.86$	$3.37 \pm 1.32$	$1.78 \pm 0.84$	$1.37 \pm 0.00$		
trans-Nonachlor	$4.00 \pm 1.00$	$3.37 \pm 1.39$ 7 58 $\pm 4.45$	$4.28 \pm 0.91$	3.49±1.10 9.03±3.44		
HCB	$9.32 \pm 4.33$ 0.81 + 0.44	$1.58 \pm 4.45$ 0.60 ± 0.34	$9.39 \pm 1.00$	$0.03 \pm 2.00$		
Dieldrin	$5.67 \pm 3.07$	$0.09 \pm 0.04$ 5 24 $\pm$ 2 76	$0.80 \pm 0.20$	$0.00 \pm 0.29$		
Hentashlar anavida	$1.22 \pm 0.67$	$3.24 \pm 3.70$	$0.38 \pm 2.82$	$4.58 \pm 1.82$		
Toxanhana	$1.33 \pm 0.07$	$1.28 \pm 0.71$	$1.09 \pm 1.14$	1.49 ± 1.10		
Total DCPa	36.1 ± 12.4	$43.1 \pm 10.0$	49.4 ± 4.5	42.8±0.7		
Total PCDs	84.4 ± 32.8	09.3±43.0	$85.7 \pm 24.1$	12.9±21.3		
		Lake Michig	an (lean trout)			
<i>p,p</i> ′- <b>DD</b> T	$11.8 \pm 3.0$	$10.5 \pm 3.4$	$8.46 \pm 4.40$	$6.83 \pm 3.40$		
p,p'-DDE	95.1 ± 19.3	$86.6 \pm 16.7$	$65.8 \pm 56.8$	$56.8\pm36.0$		
p,p'-DDD	$9.27\pm3.39$	$8.21 \pm 3.27$	$5.80 \pm 2.70$	5.30 ± 2.79		
$\alpha$ -Chlordane	$9.28\pm2.63$	$8.90 \pm 2.45$	$7.09 \pm 3.72$	6.87 ± 3.76		
γ-Chlordane	$3.57 \pm 1.43$	$3.63 \pm 1.90$	$3.22 \pm 1.51$	$3.13 \pm 2.38$		
Oxychlordane	$3.19 \pm 0.90$	$2.84 \pm 0.89$	$2.00 \pm 1.18$	$1.79 \pm 1.21$		
cis-Nonachlor	$8.10 \pm 1.81$	$6.63 \pm 1.43$	$5.29 \pm 3.68$	$4.78 \pm 2.50$		
trans-Nonachlor	$19.3 \pm 6.7$	$18.9 \pm 6.0$	$14.2 \pm 7.5$	$12.9 \pm 7.1$		
HCB	$1.10 \pm 0.26$	$0.89 \pm 0.18$	$0.78 \pm 0.34$	$0.66 \pm 0.34$		
Dieldrin	188 + 79	$154 \pm 37$	$137 \pm 70$	128+66		
Hentachlor epoxide	$3.54 \pm 0.96$	$3.13 \pm 0.48$	$2.24 \pm 1.77$	$2.13 \pm 1.74$		
Toxaphene	$735 \pm 162$	642 + 98	49.8 + 31.8	$425 \pm 102$		
Total PCBs	$221.6 \pm 60.6$	$199.1 \pm 51.8$	$134.1 \pm 81.1$	$124.4 \pm 76.1$		
	Lake Ontario (lean trout)					
	128+28	$113 \pm 24$	8 06 + 3 36	745+305		
p, p - DD I	$12.0 \pm 2.8$	20 1 ± 17 8	$66.00 \pm 3.50$	58 2 ± 23.05		
	$91.4 \pm 14.0$	$30.1 \pm 12.8$	$00.4 \pm 20.0$	$38.2 \pm 23.0$		
	$0.78 \pm 4.60$	1.04±0.14	$7.50 \pm 0.68$	0.00 ± 0.0J		
α-Chlordane	$5.00 \pm 2.00$		$4.72 \pm 1.97$	ND		
y-Chiordane	1.71±0.96		$1.42 \pm 0.73$	ND		
Jxycniordane	$1.50 \pm 0.51$	ND	$1.34 \pm 0.51$	ND		
cus-Nonachlor	$5.04 \pm 2.07$	ND	$4.23 \pm 1.55$	ND		
trans-Nonachior	15.6 ± 6.1	ND	$13.0 \pm 4.6$	ND		
HCR	$2.63 \pm 1.26$	$2.38 \pm 0.94$	$2.15 \pm 0.81$	$1.79 \pm 0.69$		
Dieldrin	$7.20 \pm 2.64$	0.93±2.45	$5.54 \pm 1.62$	$5.11 \pm 1.62$		
Heptachlor epoxide	$1.16 \pm 0.38$	ND	$0.93 \pm 0.28$	ND		
Toxaphene	$25.7 \pm 14.7$	$7.4 \pm 6.41$	21.7±8.9	ND		
Fotal PCBs	$208.8 \pm 90.8$	$186.5 \pm 81.4$	$180.5 \pm 58.6$	$159.3 \pm 55.2$		
		Lake Superior (f	at trout/siscowet)			
₽,₽'-DDT	$7.25 \pm 3.94$	4.21 ± 1.15	$13.3 \pm 14.9$	$3.75 \pm 1.35$		
p,p'-DDE	$52.4 \pm 28.1$	$41.8 \pm 14.5$	84.4 ± 92.0	75.9 ± 92.2		
p,p'-DDD	$3.96 \pm 0.79$	$3.28\pm0.52$	$3.46 \pm 1.44$	$2.99 \pm 1.12$		
x-Chlordane	$4.26 \pm 0.90$	$3.82 \pm 1.13$	$3.83 \pm 1.02$	3.61 ± 0.99		
y-Chlordane	$1.59 \pm 0.37$	$1.40 \pm 0.51$	$1.60 \pm 0.38$	$2.07 \pm 0.84$		
Oxychlordane	$4.36 \pm 1.21$	3.96±0.77	$4.75 \pm 2.75$	3.88±1.86		
cis-Nonachlor	$10.22 \pm 3.08$	$8.47 \pm 1.86$	$10.76 \pm 6.02$	$8.51 \pm 3.91$		
trans-Nonachlor	$4.36 \pm 1.21$	$3.96 \pm 0.77$	$20.06 \pm 9.09$	$16.36 \pm 7.40$		
HCB	$0.82 \pm 0.25$	$0.69 \pm 0.16$	$0.72 \pm 0.29$	$0.55 \pm 0.12$		
Dieldrin	423 + 248	$3.60 \pm 2.00$	$4.30 \pm 1.63$	$3.61 \pm 1.79$		
Heptachlor epoxide	$2.66 \pm 2.37$	$1.15 \pm 0.48$	$0.92 \pm 0.37$	$0.95 \pm 0.36$		
Toxaphene	3134 + 1520	$225.6 \pm 8.7$	359.5 + 232.9	$198.1 \pm 72.9$		
	J.J. ( ± 102.0					

*n* = 3

Ave. fillet wt. Baked: LH, raw 205.8 g, ckd 158.6 g; LM, raw 212.6 g, ckd 174.7 g; LO, raw 228.8 g, ckd 189.5 g; LS, raw 171.7 g, ckd 127.7 g. Charbroiled: LH, raw 206.7 g, ckd 156.2 g, LM, raw 191.6 g, ckd 151.7 g; LO, raw 216.7 g, ckd 174.3 g; LS, raw 151.0 g, ckd 149.5 g.

	Lake M	ichigan	Lake Si	Lake Superior	
Compounds	Raw	Cooked	Raw	Cooked	
		I	Baked		
n.n'-DDT	$11.84 \pm 3.04$	$10.47 \pm 3.44$	7 25 + 3 94	421+115	
<i>p.p</i> ′-DDE	$95.1 \pm 19.3$	$86.6 \pm 16.7$	$52.4 \pm 28.1$	$41.8 \pm 14.5$	
p.p'-DDD	$9.27 \pm 3.39$	$8.21 \pm 3.27$	$3.96 \pm 0.79$	$3.28 \pm 0.52$	
$\alpha$ -Chlordane	$9.27 \pm 2.63$	$8.90 \pm 2.45$	$4.26 \pm 0.90$	$3.82 \pm 1.13$	
$\gamma$ -Chlordane	$3.51 \pm 1.44$	$3.63 \pm 1.90$	$1.59 \pm 0.37$	$1.40 \pm 0.51$	
Oxychlordane	$3.19 \pm 0.90$	$2.84 \pm 0.89$	$4.36 \pm 1.21$	$3.96 \pm 0.77$	
cis-Nonachlor	$8.10 \pm 1.81$	$6.63 \pm 1.43$	$10.22 \pm 3.08$	$8.47 \pm 1.86$	
trans-Nonachlor	$19.27 \pm 6.71$	$18.86 \pm 6.03$	$4.36 \pm 1.21$	$3.96 \pm 0.77$	
НСВ	$1.10 \pm 0.26$	$0.89 \pm 0.18$	$0.82 \pm 0.25$	$0.69 \pm 0.16$	
Dieldrin	$18.78 \pm 7.89$	$15.44 \pm 3.72$	$4.23 \pm 2.48$	$3.60 \pm 2.00$	
Heptachlor epoxide	$3.54 \pm 0.96$	$3.13 \pm 0.48$	$2.66 \pm 2.37$	$1.15 \pm 0.48$	
Toxaphene	$73.5 \pm 16.2$	$64.1 \pm 9.8$	$313.4 \pm 152.0$	$225.6 \pm 8.7$	
Total PCBs	$221.6 \pm 60.6$	199.1 ± 51.8	$153.1 \pm 106.4$	$125.3 \pm 90.4$	
		Cha	rbroiled		
<i>p,p</i> ′-DDT	$8.46 \pm 4.40$	$6.83 \pm 3.90$	$13.26 \pm 14.96$	$3.75 \pm 1.35$	
p,p'-DDE	$65.8 \pm 25.3$	$56.8 \pm 36.0$	$84.4 \pm 92.0$	$75.9\pm92.2$	
p,p'-DDD	$5.80 \pm 2.70$	$5.30 \pm 2.79$	$3.46 \pm 1.44$	$2.99 \pm 1.12$	
$\alpha$ -Chlordane	$7.09 \pm 3.72$	$6.87 \pm 3.76$	$3.83 \pm 1.02$	$3.61 \pm 0.99$	
$\gamma$ -Chlordane	$3.22 \pm 1.51$	$3.13 \pm 2.38$	$1.60 \pm 0.38$	$2.07 \pm 0.85$	
Oxychlordane	$2.00 \pm 1.18$	$1.79 \pm 1.21$	$4.75 \pm 2.75$	$3.88 \pm 1.86$	
cis-Nonachlor	$5.29 \pm 3.68$	$4.78 \pm 2.50$	$10.76 \pm 6.02$	$8.51 \pm 3.91$	
trans-Nonachlor	$14.2 \pm 7.5$	$12.9 \pm 7.1$	$20.1 \pm 9.1$	$16.4 \pm 7.4$	
HCB	$0.78 \pm 0.34$	$0.66 \pm 0.34$	$0.72 \pm 0.30$	$0.55 \pm 0.12$	
Dieldrin	$13.69 \pm 7.04$	$12.80 \pm 6.61$	$4.30 \pm 1.63$	$3.61 \pm 1.79$	
Heptachlor epoxide	$2.24 \pm 1.77$	$2.13 \pm 1.75$	$0.92 \pm 0.37$	$0.95 \pm 0.37$	
Toxaphene	$50.0 \pm 31.8$	$42.5 \pm 19.2$	$359.5 \pm 232.9$	$198.0 \pm 72.9$	
Total PCBs	134.1±81.1	$124.4 \pm 76.1$	$135.9 \pm 117.3$	$92.6 \pm 74.3$	
		Sal	lt Boiled		
<i>p</i> , <i>p</i> ′-DDT	$16.67 \pm 3.56$	$16.79 \pm 5.08$	$6.61 \pm 2.63$	$5.58 \pm 2.24$	
p,p'-DDE	$130.6 \pm 49.4$	$121.4 \pm 44.0$	$53.5 \pm 18.9$	$40.2 \pm 9.0$	
p,p'-DDD	$12.11 \pm 4.16$	$11.54 \pm 4.30$	$5.13 \pm 1.81$	$4.22 \pm 1.07$	
$\alpha$ -Chlordane	$13.11 \pm 3.17$	$12.41 \pm 3.29$	$7.19 \pm 2.13$	$5.48 \pm 1.69$	
$\gamma$ -Chlordane	$5.70 \pm 1.23$	$5.65 \pm 1.29$	$2.78 \pm 0.87$	$2.01 \pm 0.56$	
Oxychlordane	$3.91 \pm 1.77$	$3.80 \pm 1.60$	$6.13 \pm 2.25$	$4.76 \pm 1.66$	
cis-Nonachlor	$11.24 \pm 3.02$	$10.13 \pm 3.81$	$11.11 \pm 1.36$	$9.93 \pm 2.59$	
trans-Nonachlor	$29.1 \pm 10.2$	$25.4 \pm 11.9$	$20.6 \pm 7.7$	$18. \pm 4.5$	
HCB	$1.27 \pm 0.13$	$1.18 \pm 0.25$	$1.44 \pm 0.57$	$0.90 \pm 0.35$	
Dieldrin	$21.32 \pm 3.16$	$17.91 \pm 2.33$	$8.73 \pm 4.16$	$7.64 \pm 3.44$	
Heptachlor epoxide	$3.91 \pm 0.47$	$3.81 \pm 0.69$	$2.02 \pm 0.65$	$1.81 \pm 0.74$	
Toxaphene	$99.2 \pm 19.7$	$94.3 \pm 24.6$	343.5±98.9	$286.1 \pm 93.2$	
Total PCBs	$301.5 \pm 119.7$	272.7 ± 118.3	$119.2 \pm 27.5$	$96.6 \pm 24.3$	
(		Si	moked		
<i>p,p</i> ′-DDT	$30.1 \pm 13.8$	$12.7 \pm 6.9$	$27.2 \pm 6.1$	$9.8 \pm 1.2$	
p,p-DDE	$196.7 \pm 116.4$	$103.8 \pm 74.1$	$131.8 \pm 53.2$	$77.1 \pm 18.3$	
p,p'-DDD	$26.7 \pm 15.3$	$10.4 \pm 6.9$	$14.4 \pm 3.2$	$8.0\pm0.9$	
α-Chiordane	$25.0 \pm 12.1$	$12.4 \pm 7.5$	$20.2 \pm 6.4$	$11.5 \pm 2.2$	
$\gamma$ -Chlordane	$12.17 \pm 5.52$	$6.20 \pm 3.54$	$6.36 \pm 2.00$	$3.82 \pm 1.06$	
Oxychlordane	$7.61 \pm 4.78$	3.27 ± 2.67	16.20±8.98	$5.97 \pm 1.63$	
cis-Nonachlor	$19.3 \pm 12.7$	$9.5 \pm 6.6$	$36.7 \pm 12.7$	$20.2 \pm 4.4$	
trans-Nonachlor	$46.7 \pm 25.7$	$21.1 \pm 15.0$	$68.8 \pm 24.3$	$37.8 \pm 7.3$	
HCB	$2.68 \pm 1.39$	$1.27 \pm 0.84$	$3.92 \pm 0.83$	$2.11 \pm 0.12$	
Dielarin	$41.10 \pm 25.9$	$24.0 \pm 16.9$	$23.3 \pm 6.5$	$13.8 \pm 1.4$	
Heptachior epoxide	$11.31 \pm 6.77$	$4.68 \pm 3.49$	$5.25 \pm 0.98$	$3.40 \pm 0.18$	
Total DCD	1/8.1 ± 10/.6	91.5±61.2	1114.7±524.2	$62/.0 \pm 119.4$	
iotai rubs	421.0±204./	$24/./\pm 18/.0$	$299.6 \pm 124.3$	$188.6 \pm 38.1$	

# Table 3. Pesticides and total polychlorinated biphenyls (PCBs) expressed as micrograms in per raw and baked charbroiled, salt boiled or smoked lake trout fillet harvested from Lakes Michigan (lean) and Superior (fat/siscowets)

n = 3.

Ave. fillet wt. Lake Michigan, BK raw 212.6 g, ckd 174.7 g, CB raw 191.6 g, ckd 151.7 g, SB raw 245.3 g, ckd 215.6 g; SM raw 564.5 g, ckd 327.7 g. Lake Superior, BK raw 171.7 g, ckd 127.7 g; CB raw 151.0 g, ckd 113.3 g; SB raw 178.3 g, ckd 154.8 g, SM raw 278.3 g, ckd 149.5 g.



Baked Charbroiled 🖾 Salt boiled 🖾 Smoked



about 30% but ranged from a low average loss of 21% for dieldrin to a high average loss of 39% for the chlordane complex. The lowest percentage of loss of pesticides during pan-frying white bass was also for dieldrin (17%) (Zabik et al., 1995b). These losses of pesticides from lake trout compare very well with average losses of the DDT complex of 30.4 and 33.1% for chinook salmon and carp, respectively, which had been found in another segment of the study (Zabik et al., 1995a) but was less than the 64-72% that had been reported for lake trout by Reinert et al. (1972) however this early study used skin-on untrimmed fillets. Nevertheless, Smith et al. (1973) had reported only minimum losses of DDT compounds (2-16%) during baking or poaching chinook salmon. A later study of the effect of broiling, roasting and cooking by microwave on DDT compound reduction from fat lake trout (siscowets) (Zabik et al., 1979) found losses of 30-57%.

The average loss of dieldrin of 37 and 54% for chinook salmon and carp, respectively (Zabik *et al.*, 1995*a*), agrees with the loss of 25-57% from fat lake trout (Zabik *et al.*, 1979) but were higher than the 21% found for lake trout in the current paper.

Some early studies showed inconsistent or minimal losses of pesticides and PCBs (Cin & 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 39–53% while roasting or cooking by microwave resulted in more varied losses ranging from 25 to 54% (Zabik *et al.*, 1979).

Sherer and Price (1993) used a mass basis to summarize PCB loss from many of earlier studies. By this method they reported an average of 22% PCB loss by baking chinook salmon, lake trout, smallmouth bass and bluefish; 27% loss from broiling lake trout and brown trout; a 56% loss from frying smallmouth bass and white croaker and a 26% loss from microwaving lake trout. The current study had an average loss of 23% for total



Fig. 2. Average percentage reduction of pesticides and total PCBs during cooking/processing lake trout and siscowets from the Great Lakes.

PCBs that is at the low end of previous reports and lower than the 41% PCBs reduction from chinook salmon and 33% from carp (Zabik *et al.*, 1995*a*) but were intermediate to the 18% loss of total PCBs for walleye and the 28% loss from white bass (Zabik *et al.*, 1995*b*).

#### Polynuclear aromatic hydrocarbons

Polynuclear aromatic hydrocarbons were analyzed in the raw fish that was to be smoked as well as in the smoked fillets. These values are included in Table 4. Although it is well documented that polynuclear aromatic hydrocarbons are formed during the smoking of foods, there is little information on the level of polynuclear aromatic hydrocarbons in either raw or smoked fish. Of the polynuclear aromatic hydrocarbons analyzed, pyrene was found in the highest level in the raw skin-on fillets. This was also found for various species of Lake Ontario fish (Lawrence & Weber, 1984a). These authors reported the total level of 11 polynuclear aromatic hydrocarbons ranged from 2.1 ng/g for crappies to 7.9 ng/g for eel. The authors attributed the relatively low levels of total polynuclear aromatic hydrocarbons in the raw fish to the vertebrate fish's ability to rapidly metabolize polynuclear aromatic hydrocarbons. The total polynuclear aromatic hydrocarbons in the raw lake trout and siscowets in the current study are in this range. Air (Lawrence & Weber, 1984b) and soil (Huntley et al., 1993) can lead to contamination of polynuclear aromatic hydrocarbons in raw foods.

Various levels of polynuclear aromatic hydrocarbons have been found by two studies that quantitated polynuclear aromatic hydrocarbons in smoked fish products. Lawrence and Weber (1984*a*) found smoked herring had a total of 30.5 ng/g PAHs (based on nine compounds). In an extensive study of 37 polynuclear aromatic hydrocarbons compounds in smoked Nigerian freshwater fish, Afolabi *et al.* (1983) reported that the total PAH content of traditionally smoked fish ranged from 1164 to 2237 ng/g of fish dry weight. On a dry weight basis, the

2	23	7

Table 4	Polynyclear aromatic	hydrocarhons (ng/g	wet tissue) in ray	v and smoked trout he	arvested from Lake	s Michigan and Superior
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	Lake Mi	chigan (lean)	Lake Superior (fat/siscowet)	
compounds	Raw	Smoked	Raw	Smoked
Naphthalene (Range)	ND	$0.92 \pm 0.38$ (0.41 - 1.46)	ND	$2.49 \pm 0.70$ (1.64 - 3.60)
Acenaphthylene (Range)	ND	$\begin{array}{c} 0.11 \pm 0.04^{d} \\ (0.07 - 0.16) \end{array}$	ND	0.13 <sup>a</sup>
Acenaphthene Fluorene	ND ND	ND 1.51 ± 0.03 (0.92-1.92)	ND ND	ND 3.09±0.46 (2.45-3.62)
Phenanthrene	ND	8.35 ± 1.33 (6.09 - 10.03)	$0.07 \pm 0.02^d$ (0.05 - 0.08)	$7.61 \pm 1.73$ (5.29-10.11)
Anthracene (Range)	ND	$1.09 \pm 0.14$ (0.91 - 1.26)	$0.06 \pm 0.02^{e}$ (0.04-0.08)	$1.66 \pm 0.85$ (0.49 - 2.71)
Fluoranthene (Range)	$0.39 \pm 0.25^{e}$ (0.21 - 0.82)	$26.84 \pm 3.53$ (22.87 - 31.46)	$0.13 \pm 0.03^{e}$ (0.11-0.18)	$38.68 \pm 6.60$ (30.63-45.77)
Benzo[b]fluoranthene Pyrene (Range)	ND 0.84±0.31 (0.43-1.24)	0.08" 82.40 ± 11.18 (63.99 - 95.46)	ND 2.91 ± 0.51 (2.46 - 3.86)	ND 175.43 ± 37.07 (110.29 - 220.41)
Benzo[a]fluorene (Range)	ND	$0.88 \pm 0.29$ (0.47 - 1.21)	0.09 <sup>a</sup>	$1.60 \pm 0.33$ (1.11 - 1.94)
Benzo[b]fluorene (Range)	$0.10 \pm 0.02^{b}$ (0.06-0.12)	$1.27 \pm 0.34$ (0.84 - 1.76)	$0.20 \pm 0.04$ (0.16-0.25)	$0.71 \pm 0.23$ (0.41-0.96)
3, 6-Dimethylphenanthrene (Range)	$\begin{array}{c} 0.11 \pm 0.04^d \\ (0.06 - 0.15) \end{array}$	1.48 ± 0.29 (1.16 – 1.82)	$0.15 \pm 0.08$ (0.06-0.28)	$2.04 \pm 0.68$ (0.95 - 2.92)
Benz[a]anthracene (Range)	$\begin{array}{c} 0.17 \pm 0.07^{d} \\ (0.06 - 0.26) \end{array}$	$9.66 \pm 0.60$ (8.92 - 10.54)	$1.54 \pm 0.32$ (1.02 - 1.88)	$15.63 \pm 2.10$ (12.07 - 17.88)
Perylene (Range)	ND (1.19-2.89)	$1.84 \pm 0.61$ (0.51 - 0.94)	0.1 <i>5</i> <sup><i>a</i></sup>	$0.73 \pm 0.17$
Benzo[a]pyrene (Range)	ND (4.28-6.64)	$5.12 \pm 0.81$ (6.22 - 10.27)	ND	8.43 ± 1.35
Benzo[e]pyrene Dibenz[ac]anthracene (Range)	ND ND	ND 1.30±0.34 (0.91-1.82)	ND $0.41 \pm 0.16$ (0.22 - 0.62)	ND 1.47±0.30 (1.07-1.86)
Dibenz[ah]anthracene (Range)	ND	$3.21 \pm 0.91$ (1.66-4.26)	ND	3.99±0.39 (3.39-4.53)
Picene (Range)	ND	$0.81 \pm 0.17$ (0.61 - 1.08)	ND	2.89±0.92 (1.95-4.22)
Ideno[1,2,3-cd]pyrene (Range)	ND	4.17±0.72 (3.38-5.01)	ND	$2.00 \pm 0.57$ (0.97 - 2.54)
Anthanthrene Dibenzo[ae]pyrene (Range)	0.08" ND	ND $0.53 \pm 0.17^{e}$ (0.38 - 0.82)	ND 0.14±0.04 <sup>c</sup> (0.10-0.17)	ND 0.36±0.20 <sup>e</sup> (0.17-0.65)
9, 10-Diphenylanthracene Dibenzo[ai]pyrene Dibenzo[ah]pyrene (Range)	ND ND ND	0.08 <sup>a</sup> ND ND	ND ND $0.64 \pm 0.45^{e}$ (0.14 - 1.26)	ND ND $0.69 \pm 0.57$ (0.07 - 1.33)
Chrysene (Range)	0.07 <sup>a</sup>	$2.93 \pm 0.59$ (2.09 - 3.64)	$0.28 \pm 0.10$ (0.17-0.41)	$1.46 \pm 0.46$ (0.77 - 2.06)
Dibenzo[al]pyrene	ND	ND	ND	ND
TOTAL (Range)	$1.52 \pm 0.38$ (1.21-2.21)	$154.4 \pm 13.0$ (132.2 - 167.9)	$6.34 \pm 0.94$ (5.23 - 7.61)	270.9 ± 42.4 (199.1 - 319.6)

n=6; mean  $\pm$  standard deviation; range in parenthesis.

<sup>a</sup> Only one fillet had value > minimum detectable level. <sup>b</sup> Two samples had values > minimum detectable level.

<sup>c</sup> Three samples had values > minimum detectable level. <sup>d</sup> Four samples had values > minimum detectable level. <sup>e</sup> Five samples had values > minimum detectable level.

total PAHs in the present study ranged from 399 ng/g for smoked Lake Michigan lake trout to 647 ng/g for smoked Lake Superior siscowets. These levels were more comparable to the Nigerian researchers' Ife solar dried process which they were recommending to decrease human risk. Both studies found the level of polynuclear aromatic hydrocarbons formed during smoking was higher for fish with higher fat contents. Although the fat content of only three of the six smoked fish each from Lakes Michigan and Superior was determined, the average fat content of the smoked Lake Michigan lake trout (9.1%) was considerably lower than that of the Lake Superior siscowets (20.5%). Thus the trend in the present study supports the previous findings.

Total PAH carcinogens in the traditionally smoked Nigerian freshwater fish ranged from 204 to 571 ng/g of fish dry weight.

The level of the these PAH carcinogens [phenanthrene, anthracene, benz(a)anthracene, benzo(a)pyrene, dibenz(ac)anthracene, dibenz(ah)anthracene, ideno(1,2,3cd)pyrene, dibenzo(ae)pyrene and chrysene] in smoked Great Lakes fish in this study was 36.36 ng/g wet tissue and 42.61 ng/g wet tissue for Lake Michigan lake trout and Lake Superior siscowets, respectively. This corresponds to 94–102 ng/g based on the dry weight of the fish.

## CONCLUSION

This study has quantified the loss of organochlorine pesticides and total PCBs during processing and cooking of lake trout and siscowets of a size that represents the average size caught by sports fishermen for the lake trout or by Native American fisheries for the siscowets. Cooked lake trout fillets had significantly less residue than the corresponding raw fillets. Smoking caused a significantly greater reduction in pesticides and total PCBs but smoking also caused the formation of PAHs. Health officials will have to take both factors into account in making recommendations about whether consumers should smoke their lake trout.

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