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Effects of Cooking on Distribution Pattern and Reduction of Congener Specific Polychlorinated Biphenyls (PCBs) in Carp

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Mary E Zabik
Major professor

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EFFECTS OF COOKING ON DISTRIBUTION PATTERN AND REDUCTION OF CONGENER SPECIFIC POLYCHLORINATED BIPHENYLS(PCBs) IN CARP

By

Jeong-Hee Song

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ABSTRACT

EFFECTS OF COOKING ON DISTRIBUTION PATTERN AND REDUCTION OF CONGENER SPECIFIC POLYCHLORINATED BIPHENYLS(PCBs) IN CARP.

BY

JEONG-HEE SONG

The retentional and distributional changes of PCBs by cooking were studied with carp (*Cyprinus Carpio*) harvested from Lake Erie and Lake Huron. Carp were pan fried or deep fat fried in order to compare PCBs in raw and cooked fish. In general, since fish contain great amount of PCBs in fatty areas under skin, carp were prepared with and without skin to study the differences in concentration of PCBs.

PCBs were extracted with dichloromethane, cleaned up by GPC and florisil and silica gel chromatographic columns. The concentrations of 52 individual and total PCB congeners based on Aroclor® 1254 were analyzed by capillary column GC. The total PCBs were the summation of detectable congeners.

In this study, cooked fish exhibited the lower levels of PCBs than uncooked fish. However, the statistical

comparison (Tukey's Test) between two cooking methods showed no significant difference for the effectiveness in reducing PCB levels, even though deep fat frying was a little more effective than pan frying. The average percent reduction of total PCBs based on total micrograms per fillet was 30.2± 14.1% by pan frying, 38.1±15.6% by deep fat frying. The distribution of PCBs in carp and cooking effect on PCB homolog congeners were also determined. In both raw and cooked carp, the distribution of PCB homolog congeners was in order: penta > tetra- > hexa- > heptachlorobiphenyls. The total PCBs in skin-off carp were lower than skin-on carp.

To my parents,
Gi-Soon Choi, Jin-Gi Kim,
Myung-Hee Cho, and Ki-Jeong Song

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INTRODUCTION

It is well known that harmful chemicals are accumulated in food via concentration in the food chain from contaminated environments. Since foods are usually consumed after cooking, it is necessary to investigate the cooking effects on the concentration of harmful chemical residues in the finished product. For long time, a lot of efforts have been made to determine the level of pesticides and other environmental contaminant residues in food after processing and cooking (Liska et al., 1967; Smith et al., 1977; Trotteret al., 1989; Zabik et al., 1992).

Polychlorinated biphenyls (PCBs) are one of the chemicals which have contaminated environments and accumulated in food chain. Since Jensen (1966) identified PCBs, the concerns for PCBs in food has increased rapidly. Until 1977, PCBs were commonly used in the electrical and industrial areas. PCBs have been frequently found in rivers, lakes, of course, in the fish. PCBs are highly toxic and can cause cancer (Pal et al., 1980; Das and Kulkarni,1981; Concon, 1988; McFarland and Clarke, 1989).

Most of exposure of the general human population to

PCBs appears to be by ingestion of fish in the diet (Lands, 1986), although some PCBs ingestion has been associated with eggs and milk. Significant levels of PCBs have been discovered in fish used for human consumption in many different countries (Nelson, 1972; Schwartz et al., 1983; Seiber, 1990). PCBs may pose a health threat to consumers of fish. The diet of fresh water fish may constitute a small percentage of the total diet of consumers in the United States, however, some individuals in selected communities may consume significant amount of fresh water fish. Thus, the investigation of these chemicals in fish as eaten is necessary to lower a health threat to consumers of fish.

In the present research, the retentional and distributional changes of PCBs during cooking carp (*Cyprinus carpio*) which had been caught from Lake Erie and Lake Huron using sizes representative of those caught by sport fishermen were studied. Carp fillets were pan fried or deep fat fried in order to compare the levels of PCBs in cooked fish with those in raw fish. Also, since fish contain the chlorinated hydrocarbon chemicals in higher amounts in the fatty area under the skin (Reinert et al., 1972; Hora, 1981; Sanders and Haynes, 1988), fish samples were cooked with or without skin to investigate whether skinning reduced PCBs contents of the cooked fillets.

The objectives of this study were to determine the

effects of cooking carp (*Cyprinus carpio*) by pan frying and deep fat frying on PCB levels, and to compare the effect of two cooking methods on the reduction of congener specific PCBs commonly found in Aroclor 1254®. Also carp was cooked with and without skin to determine the effect of the skin removal from fish on reduction of those congener specific PCBs.

REVIEW OF LITERATURE

Polychlorinated Biphenyls (PCBs)

PCBs are a group of chlorinated hydrocarbons synthesized by chlorination of the biphenyl molecule. PCBs are not naturally occurring compounds. Chlorobiphenyls may carry 1 to 10 chlorine atoms with varying degrees of chlorination. There are 209 possible PCB congeners (Appendix 1). The nomenclature of chlorinated biphenyls is based on the position and extent of substitution of chlorine atoms on the biphenyl ring structure as shown in Figure 1 (The United Nations Environment Programme and the World Health Organization, 1976; Pal et al., 1980).

Usually commercial products are different mixtures of chlorobiphenyls, rather than a single pure compound. There are some kinds of commercial mixtures: Aroclor (U.S.A.), Phenoclor (France), Kanechlor (Japan), and Fenclor (Italy).

Individual manufacturers had their own system of identification for their products. In the Aroclor® series, a four digit code is used; biphenyls were generally indicated by 12 in the first two positions, while the last two numbers indicated the percentage by weight of chlorine

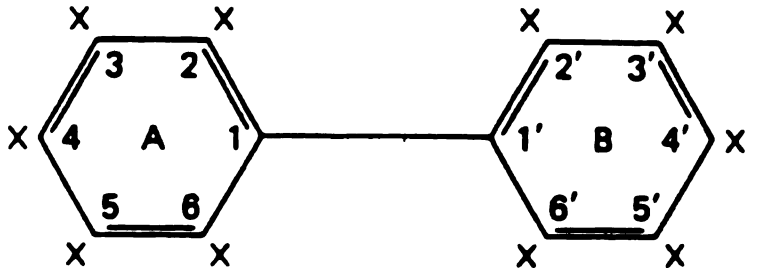


Figure 1. Biphenyl structure and numbering of carbon atoms in each ring: X represents either H or Cl depending on chlorination (Pal et al., 1980).

in the mixture. Thus, Aroclor 1254® is a polychlorinated biphenyl mixture containing 54% chlorine (The United Nations Environment Programme and The World Health Organization, 1976). The approximate composition of Aroclor 1254® is presented in Table 1.

Typical properties of PCBs are high thermal and chemical stability, low vapor pressure, high dielectric constant, high electric resistivity, high density, substantially hydrophobic and high lipophilicity. Their chemical and physical stability has been responsible for the PCB environmental contamination problem. Their melting points range from 34°C to 198°C and boiling points are usually from 275°C to 420°C (Pal et al., 1980; MacKay et al., 1983; Concon, 1988).

Historically, PCBs were first synthesized in the late 1800s, but were not used for industrial purpose in the United States until 1929. Since that time, PCBs have been distributed worldwide and accumulated in food chain from contaminated environments (Henderson et al., 1971; Kolbye, 1972; Fujiwara, 1975). All manufacturing of PCBs was prohibited after 1977 (Ghirelli et al., 1983). PCBs are accumulated in living matter, particularly in lipid tissues and organs. Most bioaccumulating PCB congeners have five to seven chlorine atoms per module. They were synthesized in

Table 1. Approximate composition of Aroclor 1254® (Pal et al., 1980)

Empirical formula	# of isomers	Composition(%)
$C_{12}H_9Cl$	3	< 0.1
$C_{12}H_8Cl_2$	12	0.5
$C_{12}H_7Cl_3$	24	1.0
$C_{12}H_6Cl_4$	42	21
$C_{12}H_5Cl_5$	46	48
$C_{12}H_4Cl_6$	42	23
$C_{12}H_3Cl_7$	24	6
$C_{12}H_2Cl_8$	12	-
$C_{12}H_1Cl_9$	3	-
$C_{12}Cl_{10}$	1	-

* The composition of Aroclor mixture was ascertained by the gas chromatographic separation.

high proportions in many Aroclor formulations and are likely to be prevalent in environment. The more highly chlorinated congeners are generally less available to organisms. Congeners with less chlorination are more readily metabolized and eliminated (Hutzinger et al., 1974; Metcalf et al., 1975; Varanasi et al., 1992).

The toxicity of PCBs varies greatly from species to species, probably as a result of differences in metabolic rates and capabilities, physiological differences, etc. The toxicity of the PCB congeners varies widely. Of the possible 209 PCB congeners, only a few - especially the planar congeners without chlorine substitution at the ortho positions of the biphenyl moiety - are demonstrably or potentially toxic (Nelson, 1972; Hutzinger et al., 1974; Safe, 1987; McFarland and Clarke, 1989). PCB congeners that are the most similar structurally to 2, 3, 7, 8 tetrachlorodibenzo-p-dioxin (TCDD) are most toxic. PCBs can cause liver damage and immunosupression, reproduction problems and birth defect etc. (Vos and Koeman, 1970; Vos, 1972; The United Nations Environment Programme and the World Health Organization, 1976; Giesy et al., 1986; Krahn et al., 1986; Kubiak et al., 1989; Park, 1991). The studies on the toxicity of PCBs have generally been conducted as laboratory or occupational exposure at high levels. Thus the degree of toxicity and effects on man has been conversable.

Factors in Reducing Polychlorinated Hydrocarbon Chemicals during Cooking

There are several factors which affect the reduction of PCBs and other chlorinated hydrocarbon pesticides during cooking. Since PCBs are polychlorinated hydrocarbons such as the pesticides, dichloro-diphenyl-trichloromethane (DDT), dieldrin and heptachlor, the factors can be considered with general chlorinated hydrocarbon chemicals or pesticides, based on the work of other researchers who have investigated the effects of cooking or processing on those harmful chemicals.

Cooking Temperature

The reduction of some chlorinated hydrocarbon pesticides by cooking was reported by Liska et al. (1967). They simmered at 88°C to 93°C for 2-3 hours or high-pressure cooked chicken at 15 psi for 3 hours. It was shown that the levels of DDT, dieldrin, and heptachlor were reduced in white meat during simmering chicken. Also, they compared the effect of temperature on heptachlor residue reduction. High temperature treatment (pressure cooking) reduced greatly the level of heptachlor in chicken meat (Table 2).

Temperature effects on chlorinated pesticide residue reduction during cooking were also investigated by Maul et

Table 2. Chlorinated pesticide residue per gram of fat in chicken meat at different temperatures (Liska et al., 1967).

	Pesticide Content (ppm)			
	Dark meat		White meat	
Pesticide	Raw	Cooked	Raw	Cooked
DDT	7.7	7.1	22.5	17.9
Dieldrin	12.6	16.6	26.0	23.3
Heptachlor(L)	6.1	6.3	9.1	6.7
Heptachlor(H)	3.8	0.7	8.4	1.6

DDT, Dieldrin : simmering at 88°C to 93°C for 2-3 hours
Heptachlor(L) : simmering at 88°C to 93°C for 2-3 hours
Heptachlor(H) : high temperature treatment, pressure cooking at 15 psi for 3 hours

al. (1971), Funk et al. (1971), and Yadrick et al. (1971). In study by Funk et al. (1971), sausage was pan fried at 204 °C and baked 177±1°C. The higher temperature cooking method, pan frying was more effective in reduction of dieldrin residue. Some of the dieldrin removed from sausage was found in the drip. Sausage samples cooked by pan frying had, in general, lower levels of dieldrin than samples cooked by baking (Table 3).

Also Hemphill et al. (1966) indicated that higher temperature cooking methods were more effective in the reduction of chlorinated hydrocarbon pesticides. The increased effectiveness of residue reduction at higher temperature might occur due to more fat loss and volatilization, in addition to heat destruction per se.

Cooking Time

Cooking time is also one of the factors affecting the reduction of chlorinated pesticides and PCBs in food. Longer cooking time might give the greater opportunity for removal of chlorinated hydrocarbon chemicals from food during cooking.

DDT in chicken tissue was reduced during heating tissues in closed containers for varying lengths of time (Ritchey et al., 1969). Only the moisture and volatile components could escape. The longer heating time appeared

Table 3. Dieldrin content in sausage, ppm based on fat (Funk et al., 1971)

Cooking Method	Sample #	Raw Sausage (ppm)	Drip (ppm)
Pan-Frying	1	23.99	11.82	16.66
	2	20.57	15.19	2.93
Baking	1	23.99	16.51	11.15
	2	20.57	18.21	3.67

Pan frying sausage at 204°C
Baking sausage at 177±1°C

to be more effective in reduction of DDT residues (Table 4).

The reduction of DDT increased as the heating time increased, even though some of DDT was converted to a metabolite, dichloro-diphenyl-dichloroethane (DDD), during the heating process. The losses of DDT residue during cooking can be also attributed to losses of residue in fat. DDT, dichloro-diphehnyl-ethane (DDE), and DDD were found to exist at relatively high levels in the fat portion of the drippings. Further study by Ritchey et al. (1972) indicated that heating alone also reduced lindane and heptachlor epoxide. Additionally, the effect of storage time on reduction of chlorinated hydrocarbons was studied with fruit and vegetable (Elkins et al., 1972). They analyzed chlorinated hydrocarbons before and after heat treatment, and also after storage 1 year at ambient and 100°F temperature (Table 5). Storage resulted in decreases of chlorinated hydrocarbons.

Fat Rendering and Cooking Surface Area

Since most of chlorinated hydrocarbon pesticides and PCBs are lipophilic, they tend to be deposited in fat tissues. Therefore, fat rendering is an important factor in reduction of chlorinated hydrocarbon chemicals in food. Fat rendering might be related to cooking temperature, cooking time, and the structure of meat tissue.

Table 4. The amounts of DDT in chicken tissues cooked for varying times (Ritchey et al., 1969)

	ppm in dry matter			
Heating time	DDT	DDE	DDD	Total
0 (raw)	31.3	11.0	3.0	45.3
30 min	22.7	9.9	5.6	38.2
60 min	14.7	9.7	11.8	36.2
90 min	9.4	9.8	14.5	33.7

Heating at 177°C for 30, 60, and 90 minutes.

Table 5. Effect of heat processing and storage on chlorinated hydrocarbon pesticides in spinach and apricots (Elkins et al., 1972)

Pesticide	Initial level (ppm)	% Reduction in residue level		
		Heat processed	Ambient 1 yr	100°F 1 yr
	Spinach			
Captan	35.7	93	100	100
Lindane	10.1	33	49	99
Thiodan	1.84	19	19	85
Toxaphene	6.50	27	60	95
Methoxychlor	12.6	21	65	100
	Apricots			
Captan	88.5	97	99	100
Lindane	6.80	13	56	100
Thiodan	1.79	13	22	85
Toxaphene	6.80	7	35	92
Methoxychlor	12.5	0	82	100

Heat processing was 65/66/252 for spinach
65/50/217 for apricots,
where the numbers are initial temperature (°F), length of process in minutes, and processing temperature (°F), respectively.

Some chlorinated pesticides and PCBs were rendered from meat into dripping. Yadrick et al. (1971), Maul et al. (1971), Morgan et al. (1971), Zabik (1974, 1979), and Shafer and Zabik (1975) compared the amount of those chemicals in broth and in meat. Most of the those chemical residue losses which occurred were attributed to fat rendering during cooking, even though significant differences of chemical losses and distribution between meat and broth occurred among meat pieces. A large portion of residue recovered was found in the broth. Great fat loss from adipose tissue contributed significantly to the loss of high proportion of chlorinated pesticides and PCBs into the broth. Therefore, fat rendering during cooking appears to be major mode of chlorinated pesticide and PCBs residues reduction in food, although there are some other differences.

It is likely that the greater surface area allows fat rendering which then reduces more chlorinated pesticide and PCBs residues from food. Thus, reduction of chlorinated pesticides and PCBs may be increased by shaping cuts to have maximum surface area. Also, surface can be exposed to higher temperature than center of meat during cooking, so that higher heat may promote more volatile and fat loss (Zabik et al., 1980). Ritchey et al. (1969) suggested cooking procedures which leached fat from the foods were most effective in reducing chlorinated hydrocarbon residues,

although long heating times were somewhat effective.

Skin and Adipose Tissue Removal

Most chlorinated pesticides and PCBs are lipid soluble. Yoshida et al. (1973) observed the elevated levels of PCBs in the skin and dark muscle of carp (*Cyprinus carpio*) due to a higher lipid content than in white muscle. Concentrations of DDT residues were highest in parts with the highest fat content in fish, such as dorsal, ventral and medial as shown in Figure 2 (Reinert et al., 1972). Also chlorinated hydrocarbon pesticide residues were at a highest concentration in the abdominal fat, less in dark meat, and least in white meat of leghorn hens (McCaskey et al., 1968).

The process which removes lipid from fish is likely to alter the PCBs and chlorinated pesticide concentrations in the fish. The effect of skin removal on the PCBs in fish fillets was determined to be used in fish advisories to help human. Removal of skin from edible portions reduced the PCBs Concentration and lipid content (Hora, 1981). The removal of skin and associated fat prior to consumption of fish is recommended to reduce the amount of chlorinated pesticides and PCBs (Zabik et al., 1979), although the effectiveness of reducing those chemicals from fish depends on the species and their fat content. Generally a loss of chlorinated pesticide and PCB residues might be directly proportional

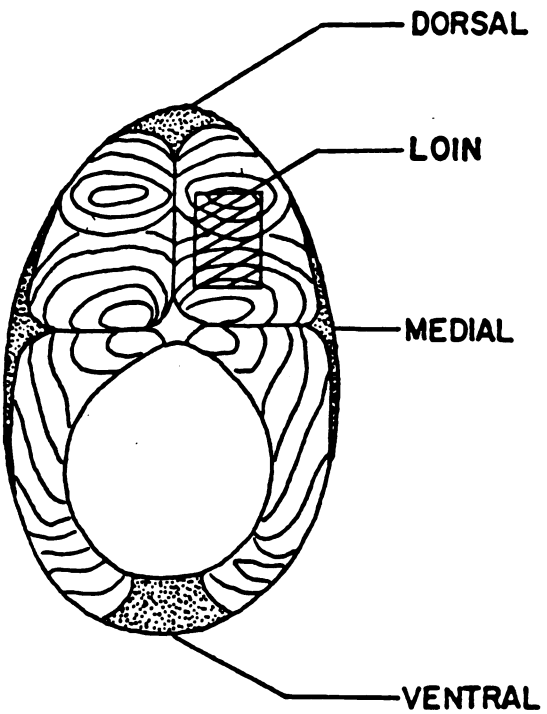


Figure 2. Portions of fish steak by cutting vertically (Reinert et al., 1972).

to the fat loss (Zabik et al., 1979; Hora, 1981; White et al., 1985; Sanders and Haynes, 1988).

Many studies showed that, in general, various cooking methods did not have significant differences in reduction of chlorinated pesticide and PCB residues in food when these cooking methods were used to cook meat to the same internal temperatures. Shafer et al. (1975) and Yadrick et al. (1972) reported that some other mode of removal such as codistillation, heat destruction, volatilization or some other unidentified factor was also responsible for losses of chlorinated pesticides and PCB residues during cooking.

Carp (*Cyprinus Carpio*)

The common carp (*Cyprinus Carpio*) seems to have originated in Central Asia. It is of major importance in Japan and India. Carp are the main type of fish grown for human consumption in Eastern Europe. Carp was introduced to North America in the nineteenth century and has distributed widely throughout most parts. Common carp in sufficient numbers are long lived. Almost any type of food is acceptable, they obtain bulk of their nourishment by sucking organic material from bottom of lakes or rivers thus they can be exposed to environmental contaminants bound to

aquatic sediments. The spawning period for carp can last from April to August, but generally spawning occurs in late May and June. The carp will continue to be a commercially important fish (EPA, 1992; Brown and Gratzek, 1980; Hepher and Pruginin, 1981).

EXPERIMENTAL PROCEDURE

Materials

Glassware Preparation

All glassware (Erlenmeyer flasks, reservoir columns, Turbo-Vap evaporator tubes, chromatographic columns and 1 mL and 5 mL volumetric flasks) were washed with detergent, rinsed with tap water, and distilled water, then with acetone, and finally with hexane. The cleaned glassware was dried in an oven.

Solvents and Reagent Preparation

Solvents: All solvents were pesticide quality.

- Hexane - 85.04%, EM Science.
- Acetone - 99.8%, Mallinckrodt Specialty Chemicals Co.
- Dichloromethane - 99.99%, Mallinckrodt Specialty Chemicals Co.
- Diethyl ether - 99.99%, Baxter Burdick & Jackson brand.
- Isooctane - 99.91%, Mallinckro

Specialty Chemicals Co.

- Petroleum ether- 99.99%, EM Science.
- Toluene - 99.99%, Mallinckrodt Specialty Chemicals Co.

Solvent mixture: Prepared by volume.

- 50% Hexane : 50% Dichloromethane
- 6% Diethyl ether in Petroleum ether
- 0.5% Toluene in Hexane

Reference PCB standard standards:

From Accustandard, New Haven, CT

Chemicals: All chemicals were pesticide quality.

- Sodium sulfate (Na_2SO_4)-granular anhydrous, activated and stored overnight at 130°C oven.
- Florisil; 60-80 mesh, activated at 130°C for 16 hours.
- Silica gel 60 ; 70-230 mesh, activated at 130°C for 16 hours.

Sample Collection and Processing

Carp were caught in Lake Erie on April 22, 1991 at 41° 51.5N, 83°20.1W near Monroe, MI and in Lake Huron in Saginaw Bay on July 22, 1991 (Figure 3). The size of fish chosen was based on the mean Creel census data from sports fishermen

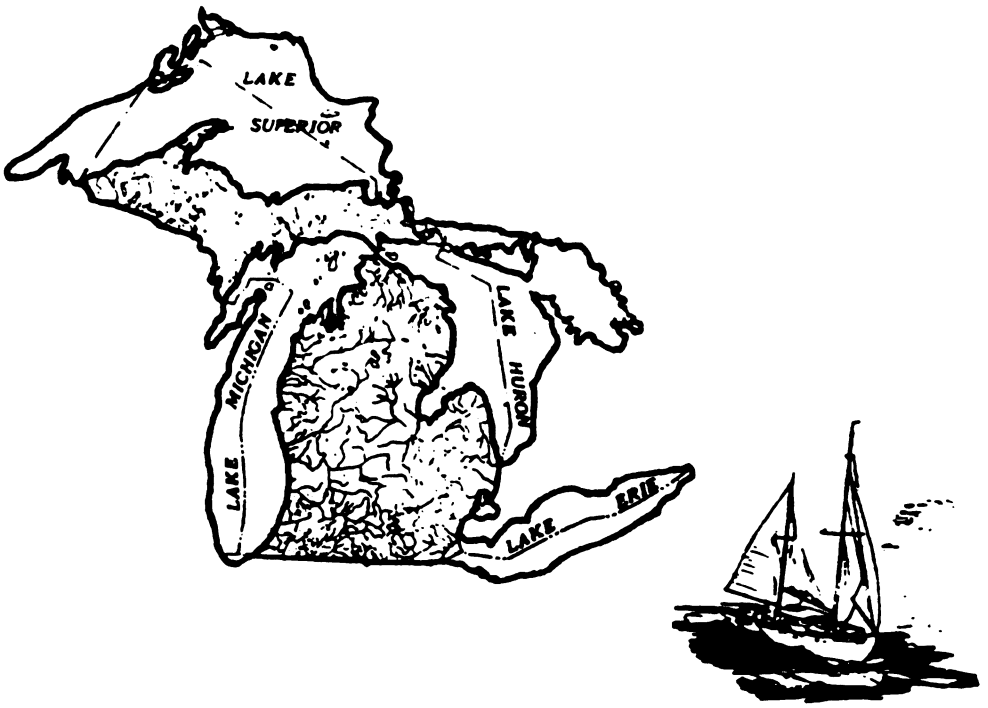


Figure 3. The sample collection: near Monroe in Lake Erie and Saginaw Bay in Lake Huron

for 1990. The average length and weight were 51.8 cm, 1834.2g in carp from Lake Erie and 46.6 cm, 1573.3g in carp from Lake Huron. In samples used in this study, half of the Lake Erie carp were male and half female. 47% of the Lake Huron carp were male and 53% were female.

All fish samples were processed within 24 hours after harvest, at the Michigan State University Meat Laboratory. Fish were processed according to recommendations to sports fishermen for trimmed skin-on or skin-off fillets (Figure 4). Each fish was scaled, deheaded, degutted and cleaned. The left side of the fish would be cooked and the right side would be used in a raw state to compare the PCBs content between raw and cooked fish. All fish contributing to skin-on fillets had the belly flap trimmed off and washed. On all fish contributing to skin-off fillets, the skin and associated fat tissue, as well as belly flap were removed. Protocols for processing the fish, in detail, are in Appendix 2. Process data included sex, length, weight and carcass yield which was based on the deheaded and degutted weight of each fish, as well as AP (As Prepared) yield. The AP yield was based on the trimmed fillet weight (Appendix 3).

$$\text{Carcass Yield } \% = \frac{\text{deheaded and degutted fish weight}}{\text{whole fish weight}} \times 100$$

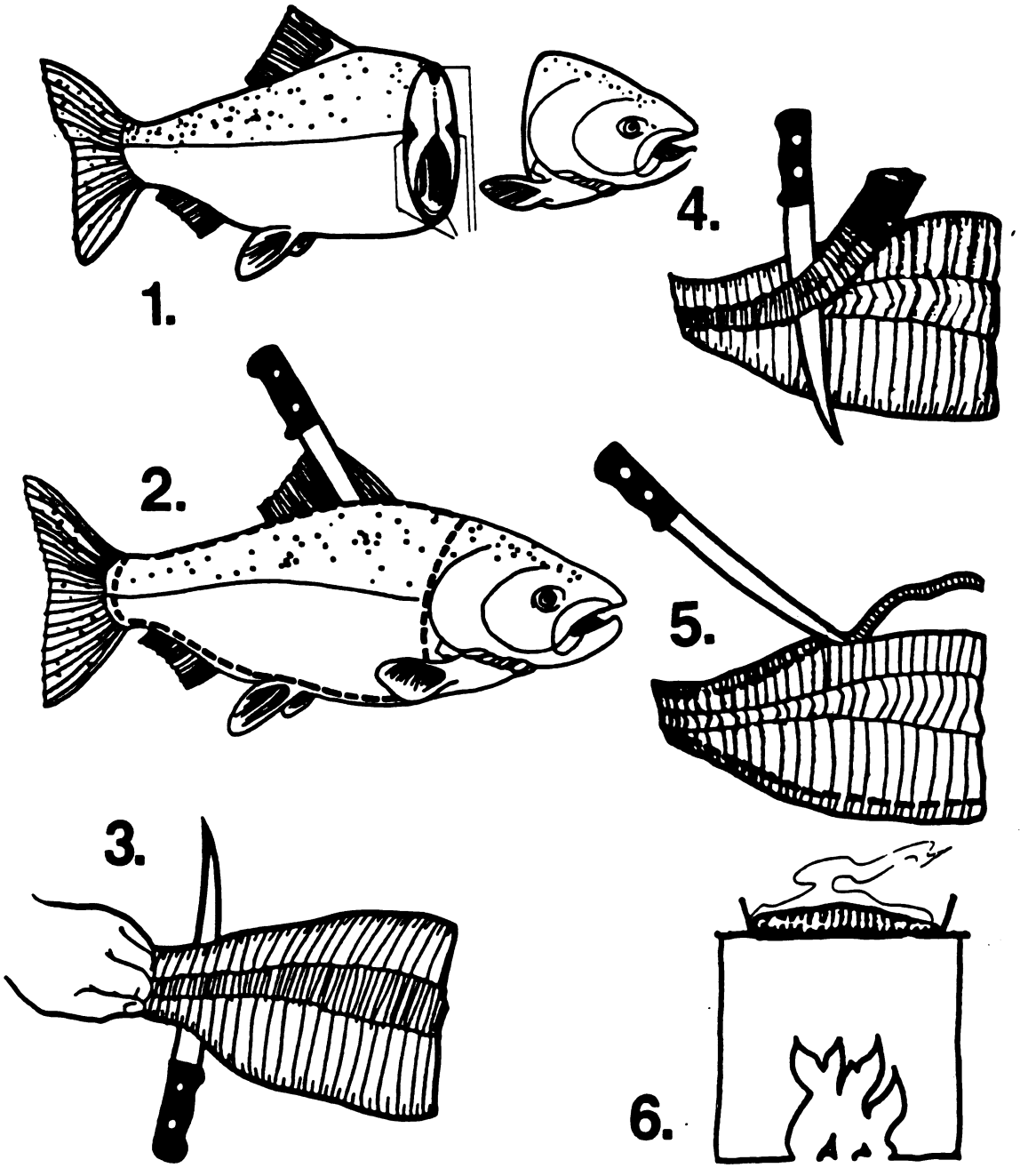


Figure 4. The procedure of fish processing and filleting. (Andrews, 1992)

$$\text{AP Yield } \% = \frac{\text{whole fish fillet weight}}{\text{whole fish weight}} \times 100$$

Sample Preparation

Preparation of Raw Sample

For the raw fish, the fillet of right side (skin-on or skin-off) was ground to a uniform particle size at a frozen state. The method of particle reduction was grinding, chopping, or blending appropriately. All raw ground fish was placed in glass containers, covered with aluminium foil, and capped. All samples were stored at -34°C.

Cooking Methods for Cooked Sample

For fish which would be in the cooked state, skin-on and skin-off fish were pan fried, according to the procedure of Puffer and Gossett (1983) or deep fat fried, according to the procedure of Morehouse and Zabik (1989). All equipment which was in contact with fish was cleaned with a cotton ball dipped into acetone after each use.

Pan Frying

A sample was removed from the freezer shortly before the pan temperature reached 175°C. Each side of fish fillet

was sprayed with no stick cooking spray (Pam®) for 3 seconds. A thermocouple was placed in the center of the thickest portion of the fish sample and a second thermocouple was placed on the surface of the frying pan to monitor the internal temperature, and to keep the frying pan at 185±5°C, respectively.

Sprayed fish fillet was placed on the frying pan, then the no stick cooking spray was sprayed lightly around the fish. If the sample was a skin-on fish fillet, the skin side was placed on the frying pan surface first. Since the fish skin acts as an insulator and keeps the temperature from increasing, cooking the skin-absent side was the last step. The fish fillet was cooked until the internal temperature reached 80°C, during which the fish piece was turned at each 20°C.

After cooking, the sample was placed on wire cooling rack for 1 minute. When a skin-on sample was used, the skin was peeled off so only the muscle tissue was analyzed as the edible portion.

Deep Fat Frying

The oil (1300±10g of Mikado, commercial soybean oil) was placed in a frying pan and heated to 180-185°C. The sample was removed from freezer just before the oil

temperature reached 150°C. A thermocouple was placed in the center of the thickest portion of the fish sample. A second thermocouple was placed in the frying oil to monitor the frying temperature and to keep it at 180±5°C. The Sample was cooked until the internal temperature reached 80±3°C, and drained in a fryer basket for 15 seconds, then on a wire rack for an additional minute.

Both pan fried and deep fat fried fish samples were homogenized or ground in an Omnimixer. Ground samples were placed in glass jars (prerinsed with acetone and hexane) and labeled. Samples were frozen and stored at -34°C.

Total cooking losses were calculated for each cooking method (Appendix 3). Fish pan fried with skin had the muscle flaked away from the skin, and the cooked muscle was weighed as the edible portion. Since deep fat fried fish are usually coated with a batter or a breading, the consumers would generally eat the skin so that the skin was included in the cooked portion. Percentage of cooking yield was based on the relation of the cooked edible weight to the raw weight (Appendix 3). Cook yield % did not contain skin except deep fat frying samples but cooking loss % contained skin.

$$\text{Cooked Yield \%} = \frac{\textbf{cooked edible weight}}{\textbf{raw fish fillet weight}} \times 100$$

$$\text{Cooking Loss \%} = \frac{\text{raw fish fillet weight - cooked fish weight}}{\text{raw fish fillet weight}} \times 100$$

Polychlorinated Biphenyl Analyses

Extraction and cleanup of samples for PCB analyses were performed using the gel permeation chromatography (GPC), florisil and silica gel chromatography. Identification and quantification of PCBs were done by gas chromatography. Capillary column gas chromatographic procedure by Ribick et al. (1982) was applied in our laboratories. The analytical procedures are summarized in Figure 5.

Lipid Extraction

Since fish contain lipids and PCBs are deposited in lipids, their samples can be extracted by techniques similar to those used for adipose tissue. Lipid extract from fish sample contains organochlorine pesticides and PCBs. The organochlorine pesticides and PCBs are non-polar compounds. In most cases, they are co-extracted together.

In column lipid extraction, fish samples were extracted with dichloromethane. The PCB congener 2,4,6 tri-chlorobiphenyl (IUPAC #30) was used as an internal standard for determination of concentrations and recoveries of PCBs.

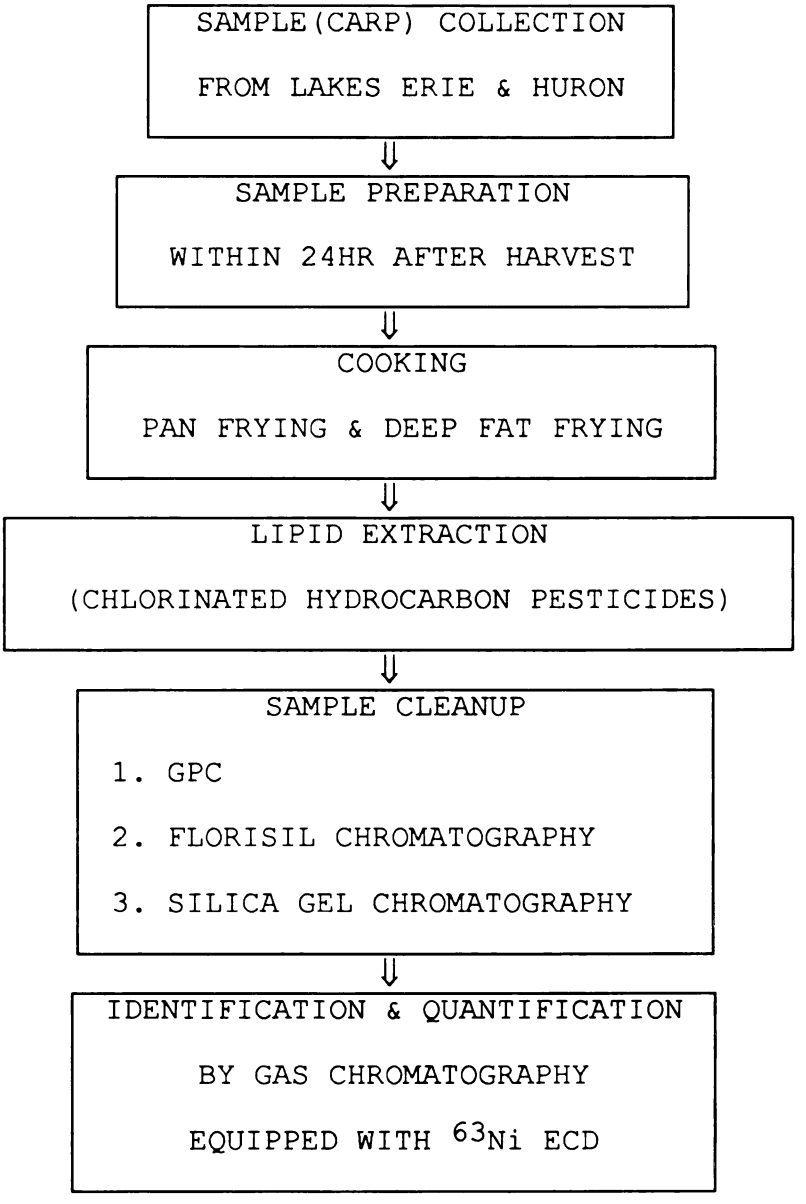


Figure 5. Overall analytical procedures for congener specific PCBs

This internal standard has not been found in the environment.

The column extraction has some advantages: less time consuming, less requirement of fragile equipment, no requirement of the multiple-solvent, and can handle numerous samples simultaneously.

The lipid extraction was accomplished by following procedure. Sample of fish (10.0g) and 1 mL of internal standard PCB (IUPAC #30, 5 ppm) was homogenized with 40g of granular anhydrous Na_2SO_4 (activated and stored overnight at 130°C) and ground to a fine powder.

The ground fish mixture was eluted in a 1 cm i.d. reservoir column with 200 mL of, dichloromethane at a flow rate of 3-5 mL/min, collected and reduced in the Turbo-Vap evaporator (Zymark) to approximately 0.5 mL volume at ambient temperature. Care was taken to avoid the dryness of extract.

The concentrated lipid extract was then diluted to 5 mL with 1:1 (v/v) hexane and dichloromethane mixture and placed in a 5 mL volumetric flask. This mixture of hexane and dichloromethane was used to promote high recoveries and to facilitate compound separation during GPC.

Cleanup of Lipid Extract

The cleanup step in an analytical procedure removes

other compounds which interfere with the determination of PCBs, prior to GC analysis.

Gel Permeation Chromatography (GPC)

Cleanup by GPC results in removal of more than 98% lipid without alteration of residue composition or levels. GPC is a form of liquid chromatography in which solute molecules are separated selectively as they permeate the pores in the column packing. The larger lipid molecules are excluded from pores because of their size, and therefore they elute from the column before the smaller contaminants do.

The automated GPC system provided for unattended operation with time control to remove lipid. Contaminant residues were collected and then a wash cycle flushed the system prior to the next sample.

The following procedure of cleanup by GPC was: 4 mL concentrated extract was put in the vial. A 2 mL aliquot of this extract was then injected into GPC column attached to a Waters/590 Programmable HPLC pump and Waters fraction collector. The lipid part was dumped and PCB portion collected, then PCB portion was reduced in a Turbo-Vap evaporator to approximately 1 mL and diluted to 5 mL with hexane. The operating conditions are presented in Appendix 4.

Florisil Column Chromatographic Cleanup

After removal of the lipids, the sample needed further cleanup to fractionate PCBs and other chlorinated hydrocarbon pesticides. Most chlorinated pesticides are eluted from a florisil column with a solvent 6% (by volume) of ethyl ether in petroleum ether. The procedure of florisil column chromatographic cleanup started column preparation. The column (1 cm i.d. x 51 cm) was prepared by placing 1 cm of granular anhydrous Na_2SO_4 on glass wool, followed by 5g of 60-80 mesh florisil (activated at 130°C for 16 hours), then 1 cm of granular anhydrous Na_2SO_4, again.

The prepared column was then washed (prewetted) with 20 mL of hexane. When the hexane reached the top of the upper layer of Na_2SO_4, the GPC concentrate was transferred to the column and allowed to drain onto a florisil bed and collected. Continuously, 40 mL of elution solvent (6% diethyl ether in petroleum ether) was added to the column. The collected eluent was reduced to approximately 5 mL volume in the Turvo-Vap evaporator (Zymark).

Silica Gel Column Chromatographic Cleanup

Silica gel column separates satisfactorily the PCBs from the majority of the remaining pesticides. The PCBs would be mainly eluted with 50 mL of 0.5% toluene in hexane.

The column was prepared the same as described for the

florisil columns but with silica gel 60 (70-230 mesh) activated at 130°C for 16 hours. A 50 mL quantity of 0.5% toluene in hexane was used as elution solvent. The eluent was reduced to approximately 0.5 mL volume in the Turbo-Vap evaporator and transferred to the 1 mL volumetric flask, using hexane to rinse the Turbo-Vap tube. The concentrate was reduced to 0.5 mL volume under a stream of N_2 gas and isooctane was added to make a final volume 1 mL.

The procedures of cleanup and separation of PCBs and other chlorinated pesticides are summarized in Figure 6.

Qualification and Quantification

Concentration of individual PCB congeners and total concentration of PCBs were determined in the PCB extract by Gas Chromatography with ^{63}Ni electron capture detector (Hewlett Packard 5890 series II), which was equipped with DB-5 capillary column (60 m x 0.25 mm i.d.). Electron capture detector is selective toward halogenated compounds. The separation from GC is effected by the interaction of the compounds with the gas (mobile phase) and liquid phase (stationary phase). The solubility in the liquid phase and volatility affect the retention times of PCB congeners. PCBs would generally elute in order of chlorination:$C_{12}H_9Cl$ first, $C_{12}Cl_{10}$ last.

The separated peaks from the GC column were detected at

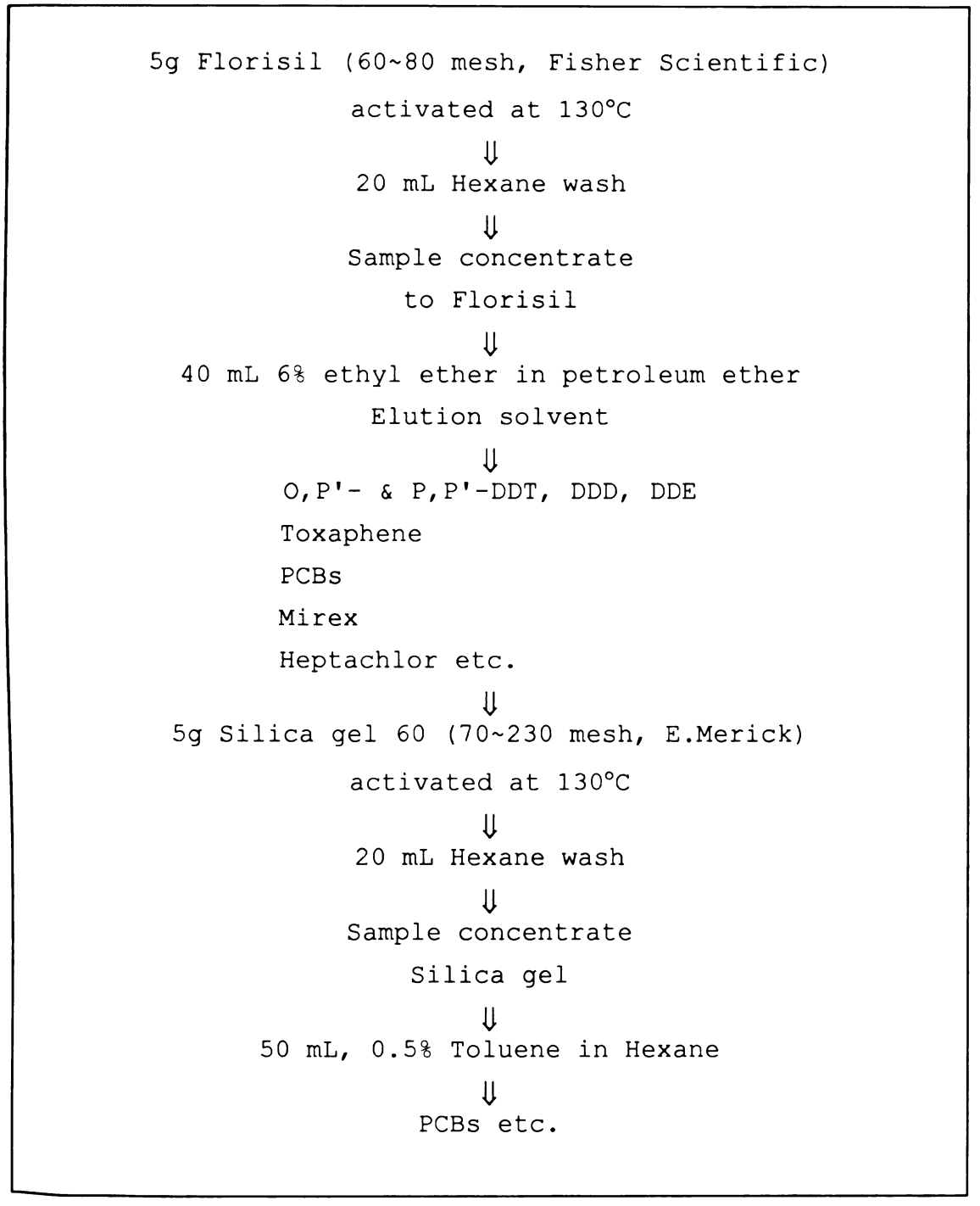


Figure 6. Cleanup and separation on procedure of PCBs and pesticides (Ribick et al., 1981)

different times (retention times). The retention time of each PCB congener was compared to the retention time of the authentic standard 52 PCB congeners based on Arochlor 1254® run under the same conditions. The standard PCB congeners used are listed in Appendix 5. The internal standard PCB congener (IUPAC #30, 2,4,6-trichlorobiphenyl) was added to correct the recovery during the entire analysis procedure. Analysis for all 209 congeners is not necessary because some PCB congeners have never been reported in environmental samples.

All quantification was based on peak areas relative to the area of individual congener standards and congener #30. A standard curve was constructed for each PCB congener from different concentrations of the standard mixture (standard/50, standard/10, standard concentration). Detector response factors were linear over a limited range. The total concentration of PCBs was determined by summing the concentrations of all of the individual congeners listed in Appendix 5 which were detected from the GC in the extract.

Final separation and quantification of PCBs were done with a Gas Chromatography, equipped with ^{63}Ni electron capture detector (ECD) under the following conditions:

Detector: 300°C

Inject: 220°C, 3 uL volume by auto sampler

Column: 60 m x 0.25 mm i.d. capillary DB-5 column

Carrier gas: He, 1 mL/min. flow rate

Oven temperature: programmed from 160°C to 280°C

Detector make-up gas: N_2

The samples were quantified by comparison of peak area determined by a computerized integrator with appropriate standards of known concentration, using following equations:

Recovery % =

$$(\text{LS of \#30 X RA of \#30}) \text{ X } \frac{1000}{\text{GPC vol. X sample wt.}}$$

Concentration =

$$\frac{\text{GLC vol. X 500 X LS of congener X RA of congener}}{\text{sample wt. X GPC vol. X Recovery \%}}$$

GPC vol.: Gas Permeation Chromatography volume (ml)
GLC vol.: Gas Liquid Chromatography volume (ml)
LS: Line Slope
RA: Retention Area
Sample wt.: Sample Weight (g)

These analyses were completed by the Pesticide Research Center at Michigan State University. All cases were replicated six times and 10% of samples were duplicated.

Statistical Analysis Procedure

The data were analyzed by general linear models (GLM) procedure, using SAS statistical software(Cary, NC). Significant differences were determined at a 0.05 level of probability using Tukey' Studentized Range Test. The main effects of variable factors (lakes, cooking methods, raw or cooked state, and skin-on or skin-off) as well as their possible interactions were considered. Statistical analyses are summarized in Appendix 6.

RESULTS AND DISCUSSION

Carp obtain the bulk of their nourishment by sucking organic materials from bottom of lakes or stream. PCBs exhibit a high affinity for particulate, and sediments are considered to be a major environmental sink for these contaminants. Young et al.(1976) and Seelye et al.(1982) found that PCBs were taken up to a great extent by mussels and fish closer to the bottom. Therefore, it is likely that the level of PCBs in carp would be relatively high.

Carp from Lakes Erie and Huron in sizes representative of those caught as sport fish, were pan fried or deep fat fried at 80°C with and without skin. After the fish fillets were cooked, the extra oil and skin (if, skin-on fillets) were discarded, except deep fat fried skin-on fish samples, prior to PCB congener analyses. Since deep fat fried fish is frequently prepared with breading or a batter and the consumer would eat them with skin, the deep fat fried skin-on fish samples were analyzed with skin.

Carp from Lake Erie were significantly larger than those from Lake Huron (Zabik et al., 1993). The average length and weight were 51.8 cm, 1834 g in carp from Lake

Erie and 46.6 cm, 1573 g in carp from Lake Huron, respectively. Carcass % and as prepared yield % (AP Yield %) of the carp are listed in Appendix 3. As expected, the average AP yield % of skin-on carp (32.7%) was significantly greater than that of skin-off carp (25.6%), even though average carcass yield % of carp which would be skinned off was significantly greater than that of skin-on carp (Zabik et al., 1993, Appendix 6-2 and 6-3).

Cooking Losses

Total cooking losses and cooking yields by pan frying and deep fat frying are summarized in Tables 6 and 7. The presence or absence of skin did not affect the cooking losses, but the cooking methods did (significance, $p < 0.05$). The total cooking losses in deep fat fried fish fillets (average 32.49%) was higher than those in pan fried fish fillets (average 19.86%). Total cooking losses varied among the various cooking methods in a previous study (Zabik et al., 1982) which used Duncan's New Multiple Range test to seek out significant differences among cooking methods. The highest cooking loss occurred in deep fat frying among the cooking methods: poaching, roasting, deep fat frying, charbroiling, and microwave cooking. They reported that a

Table 6. Total cooking loss in carp during cooking

	Total Cooking Loss (%)	
	Pan frying	Deep fat frying
With skin	21.4	31.5
Without skin	18.4	33.4
Total average	19.9	32.5

n = 12: 6 from Lake Erie, 6 from Lake Huron

Table 7. Total cooking yield in carp during cooking

	Total Cooking Yield (%)	
	Pan frying	Deep fat frying
With skin	70.7	68.4
Without skin	81.6	66.6
Total average	76.2	67.5

n = 12: 6 from Lake Erie, 6 from Lake Huron

great decrease in moisture in deep fat fried fish fillets caused the great cooking loss, even though fat was absorbed during cooking.

Cooking Effects on the Reduction of Total PCB Levels

Means and standard deviations of total PCBs levels derived from the sum of the individual congeners were expressed as ppm wet tissue (Table 8), ppm dry tissue (Table 9) in raw and cooked fillet. Generally the concentrations of PCB congeners in this report will be reported as ppm on a wet weight basis, unless specified otherwise, because most consumers are familiar with the amount of PCBs in the edible wet fish fillet more easily. Since data expressed as ppm wet tissue will not consider weight loss during cooking, data will also be presented as micrograms per fillet.

The Food and Drug Administration (FDA) regulates the tolerance level of total PCBs for fish and shellfish as 2 ppm in wet edible tissue based on packed column GC for analysis of sample. However in this study, the analysis was performed by capillary column GC. The chromatogram of capillary column improves resolution and reveals many peaks of hidden congeners as shown in Figure 7. Therefore, the capillary column approach is likely to be more accurate than

Table 8. Total PCBs expressed as ppm wet tissue in raw and cooked carp fillets

Lake	Cooking Method	Skin	PCB Content (ppm) Raw	Cooked
Erie	Pan fried	Skin-on	*1.521±0.696	1.316±0.896
		Skin-off	1.165±0.405	1.094±0.366
	Deep Fat fried	Skin-on	*3.547±2.109	3.413±1.276
		Skin-off	1.568±1.143	1.350±1.059
Huron	Pan fried	Skin-on	1.394±0.908	1.208±0.858
		Skin-off	1.583±2.106	1.395±1.962
	Deep Fat fried	Skin-on	1.598±0.949	1.188±0.721
		Skin-off	0.897±0.345	0.903±0.399

* Both total PCB levels were resulted from different portions in the same fish, although each portion of fish was randomly assigned to cooking methods.

n = 6: pan fried samples, only muscle tissue analyzed
deep fat fried samples included skin

Table 9. Total PCBs expressed as ppm in dry tissues of raw and cooked carp fillets

Lake	Cooking Method	Skin	PCB Content (ppm) Raw	Cooked
Erie	Pan fried	Skin-on	*5.905±3.068	4.147±2.664
		Skin-off	5.468±1.829	3.626±1.012
	Deep Fat fried	Skin-on	*13.47±6.930	7.659±8.363
		Skin-off	7.253±4.984	3.214±2.267
Huron	Pan fried	Skin-on	5.117±3.036	3.725±2.430
		Skin-off	5.509±5.568	3.962±4.586
	Deep Fat fried	Skin-on	6.012±3.384	2.720±3.699
		Skin-off	3.637±1.337	2.122±0.733

* Both total PCB levels were resulted from different portions in the same fish, although each portion of fish was randomly assigned to cooking methods.

n = 6: pan fried samples, only muscle tissue analyzed. deep fat fried samples included skin.

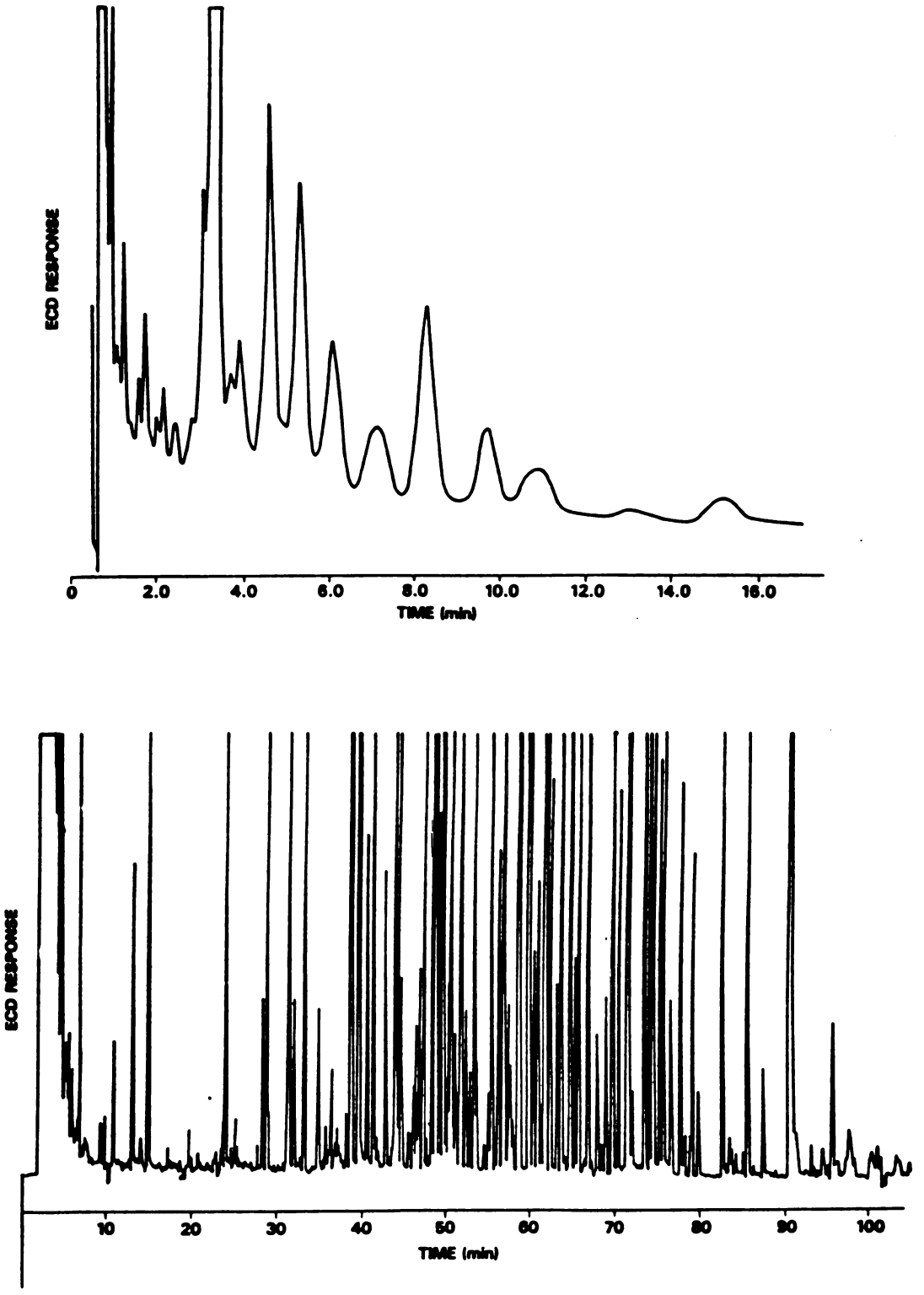
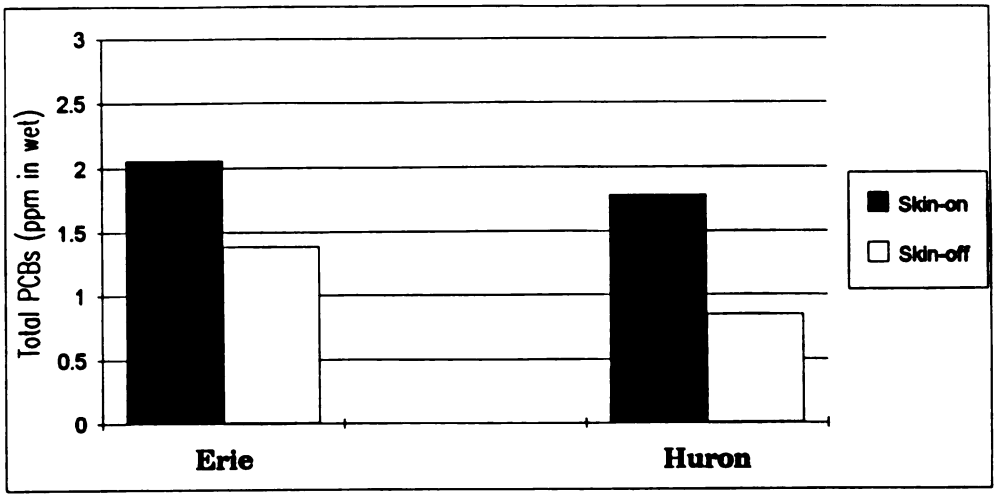


Figure 7. Exemplified chromatograms. Top, packed column; bottom, capillary column (Pellizzari et al., 1985).

the packed column approach (Pellizzari et al., 1985; Draper and Koszdin, 1991). It is likely the values by capillary column analyses would be relatively higher than those by packed column analyses (Figure 8). The average level of PCBs in skin-on fish from Lake Erie was 2.534 ppm in wet tissue. Four of the six fish from Lake Erie had higher than 2 ppm of total PCBs. Either a tail or head portion of same fish was randomly assigned to be pan fried or deep fat fried, however there were considerable variances among these portions in the same fish in Lake Erie samples. For instance, portions assigned to pan frying was 1.521 ppm of average total PCBs in wet tissue (5.905 ppm in dry tissue) but portions assigned to deep fat frying was 3.547 ppm in wet tissue (13.470 ppm in dry tissue).

The high level of total PCBs and standard deviations in skin-off raw and pan fried fish from Lake Huron were due to only one fish which showed a very high PCBs level (5.872 ppm in raw fish, 5.387 ppm in pan fried fish). The other five fish contained lower than 1 ppm in wet tissue.

The carp from Lake Erie had higher average levels of PCBs (skin-on; 2.534 ppm, skin-off; 1.367 ppm in wet tissue) than those from Lake Huron (skin-on; 1.496 ppm, skin-off; 1.240 ppm in wet tissue). The other previous studies (Thomas and Frank, 1983; Schmidt, 1989) reported that, in general, fishes from Lake Erie were more contaminated by PCBs than



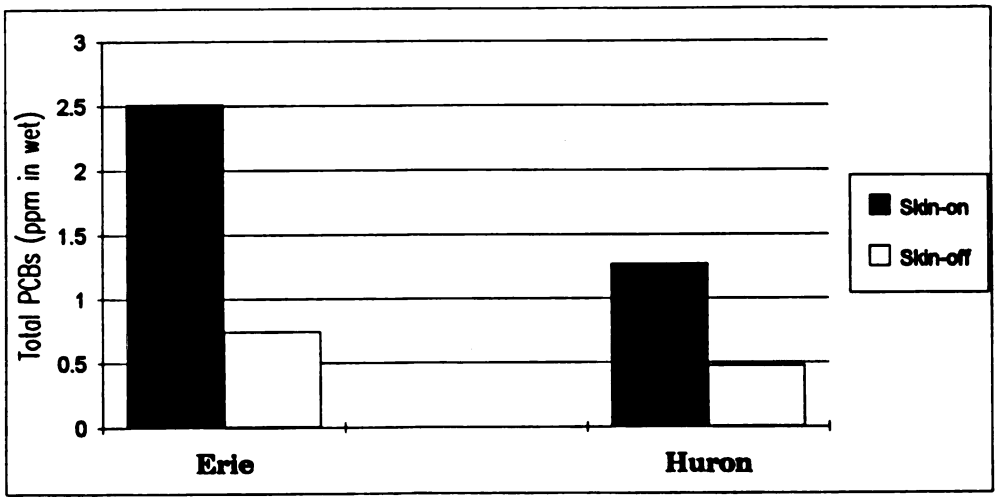


Figure 8. The average total PCBs in same carp samples from Lake Erie and Lake Huron: top, capillary column; bottom, packed column at Michigan department of Public Health (Zabik et al., 1993)

those from Lake Huron.

Generally the large fish showed the high level of total PCBs like the study by Hora (1981). The larger fish size might be partly responsible for higher level of PCBs in carp from Lake Erie. The correlation between length, weight and PCB level is presented in Figure 9-a, b, and c.

Above all, the effects of cooking on total PCBs reduction of total PCBs and PCB homolog congeners (grouped PCB congeners by chlorination) were main concerns in this experiment. It is thought that the cooking effectiveness of reducing PCBs from fish depends on the species and their fat contents. Cooking by microwave, roasting, and broiling fat lake trout (ciscowet) from Lake Superior reduced PCBs by 26-53% (Zabik et al., 1979). These fish averaged 25-29% fat. In contrast, the level of PCBs in carp harvested from Saginaw Bay, MI, with an average fat content of 7.7% was not affected by cooking (Zabik et al., 1982). The levels of PCBs in chinook and coho salmon, which were relatively low in fat, were reduced slightly by cooking (Smith et al., 1973). Fish higher in fat allowed for rendering of more fat. Thus cooking was effective in reduction of PCBs from fish.

For the current study, the average total PCB levels after cooking carp are summarized in Tables 7 and 8. Samples cooked by the two methods had the lower levels of PCBs than uncooked samples, even though the average fat content in

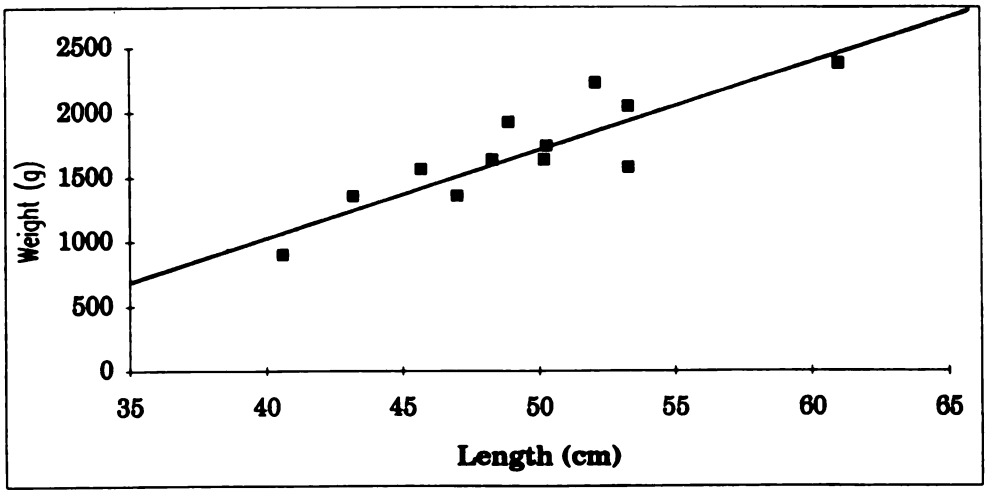


Figure 9-a. The correlation between length and weight (Correlation coefficient: 0.86)

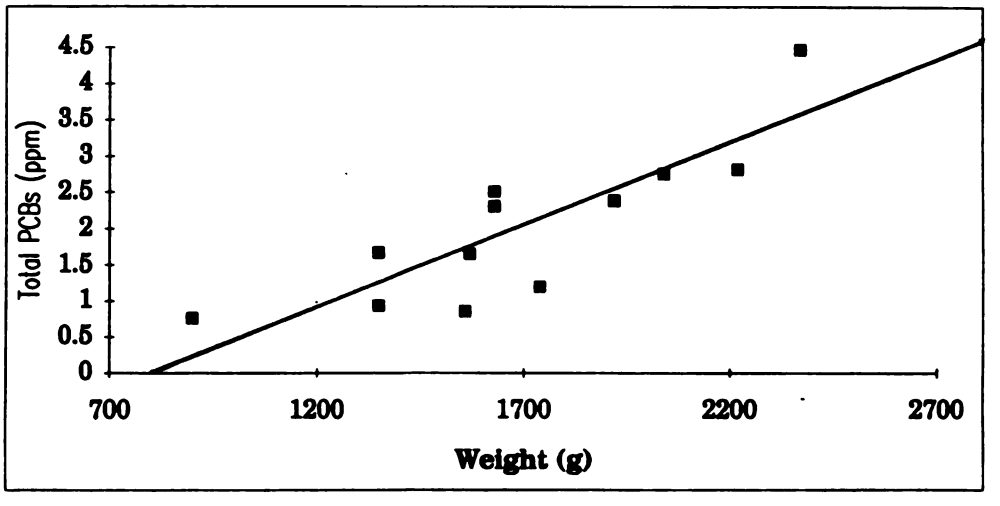


Figure 9-b. The correlation between weight and PCB level (Correlation coefficient: 0.84)

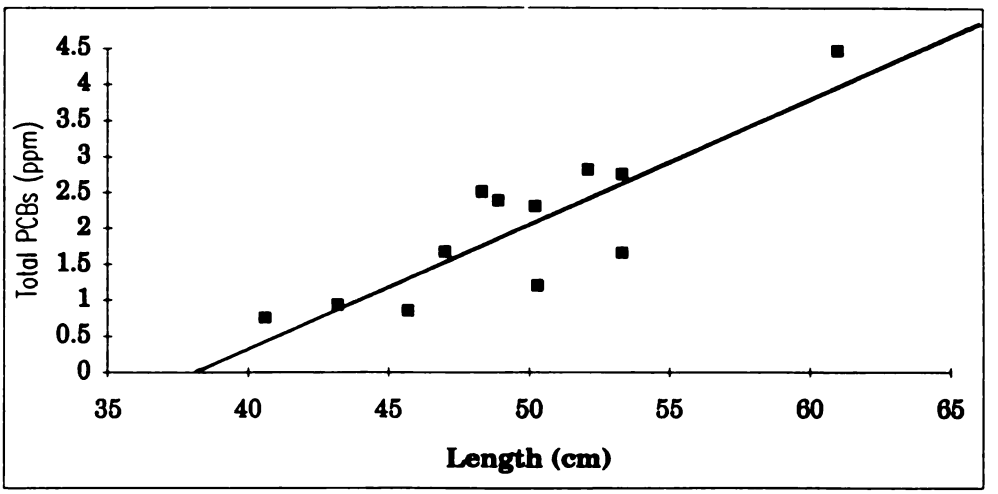


Figure 9-c. The correlation between length and PCB level (Correlation coefficient: 0.86)

these carp samples were relatively low. Lipophilic PCBs might be lost along with oil dripping and skin that was discarded after cooking.

The statistical comparisons (Tukey test) between the two cooking methods revealed no significant difference for the effectiveness in reducing PCBs levels, even though deep fat frying was a little more effective. Skea et al. (1979) reported deep fat frying reduced PCBs more effectively than other cooking methods. However, some differences in the level of total PCB congeners were related to the lakes where the carp were caught.

In order to determine the loss of PCBs during cooking, percentage reduction was determined based on the total micrograms of PCBs in raw and cooked fillets, because both fat and moisture are lost during cooking. The percentage reductions by total micrograms per fillet for all carp pieces with and without skin, are summarized in Table 10, and 11. Data expressed in Figure 10 shows the average effects of each cooking method. The percentage change of the total PCB congeners was calculated from the change in the sum of the individual congeners. Percentage change of total PCBs based on capillary column gas chromatography analyses ranged from 26% to 48% but that based on traditional packed column gas chromatography analyses by Michigan Department of Public Health (Zabik et al.,1993) ranged from 12% to 65%.

Table 10. Total PCBs expressed as micrograms per in raw and cooked carp fillets from Lake Erie and percentage reductions of PCBs by pan frying and deep fat frying.

		Total micrograms/fillet		
Cooking method	Fish	Raw	Cooked	% Change
Pan frying		Skin-on		
	1	114.59	62.35	45.59
	2	318.31	145.31	54.35
	3	122.85	90.70	26.17
	4	466.12	400.34	14.11
	5	204.46	94.89	53.59
	6	316.82	243.97	22.99
			average	36.13
		Skin-off		
	1	151.95	93.84	38.24
	2	145.50	104.57	28.13
	3	223.23	150.60	32.54
	4	113.01	89.45	20.85
	5	80.05	68.49	14.44
	6	65.81	52.24	20.62
			average	25.80
Deep fat		Skin-on		
frying	1	609.57	345.33	43.35
	2	1452.52	615.79	57.61
	3	358.84	266.85	24.59
	4	585.45	520.24	11.14
	5	179.99	159.69	11.28
	6	387.52	287.25	25.88
			average	28.98
		Skin-off		
	1	182.31	113.97	44.80
	2	137.00	77.57	50.52
	3	650.00	366.11	48.89
	4	116.23	81.12	38.90
	5	76.13	36.39	57.78
	6	61.09	39.04	44.27
			average	47.53

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

Table 11. Total PCBs expressed as micrograms per in raw and cooked carp fillets from Lake Huron and percent reductions of PCBs by pan frying and deep fat frying.

Cooking Method	Fish	Total micrograms/fillet Raw	Cooked	% Change
Pan frying		Skin-on		
	1	173.42	75.21	56.63
	2	242.14	186.08	23.15
	3	496.42	311.70	37.21
	4	36.07	24.15	33.04
	5	44.59	38.07	14.62
	6	105.92	84.53	20.20
			average	30.81
		Skin-off		
	1	55.85	31.85	42.98
	2	26.17	21.14	19.22
	3	73.74	38.72	47.49
	4	882.27	674.36	21.30
	5	56.72	52.69	7.11
	6	33.75	23.47	30.46
			average	28.09
Deep fat frying		Skin-on		
	1	148.44	77.69	47.67
	2	381.77	145.65	61.85
	3	439.34	262.22	40.31
	4	93.54	37.70	59.70
	5	58.94	42.53	27.84
	6	94.20	52.02	44.77
			average	47.02
		Skin-off		
	1	61.76	29.81	51.73
	2	31.42	26.74	14.88
	3	47.00	36.35	22.66
	4	218.76	175.54	19.76
	5	64.13	46.26	27.87
	6	59.13	37.01	37.40
			average	29.05

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

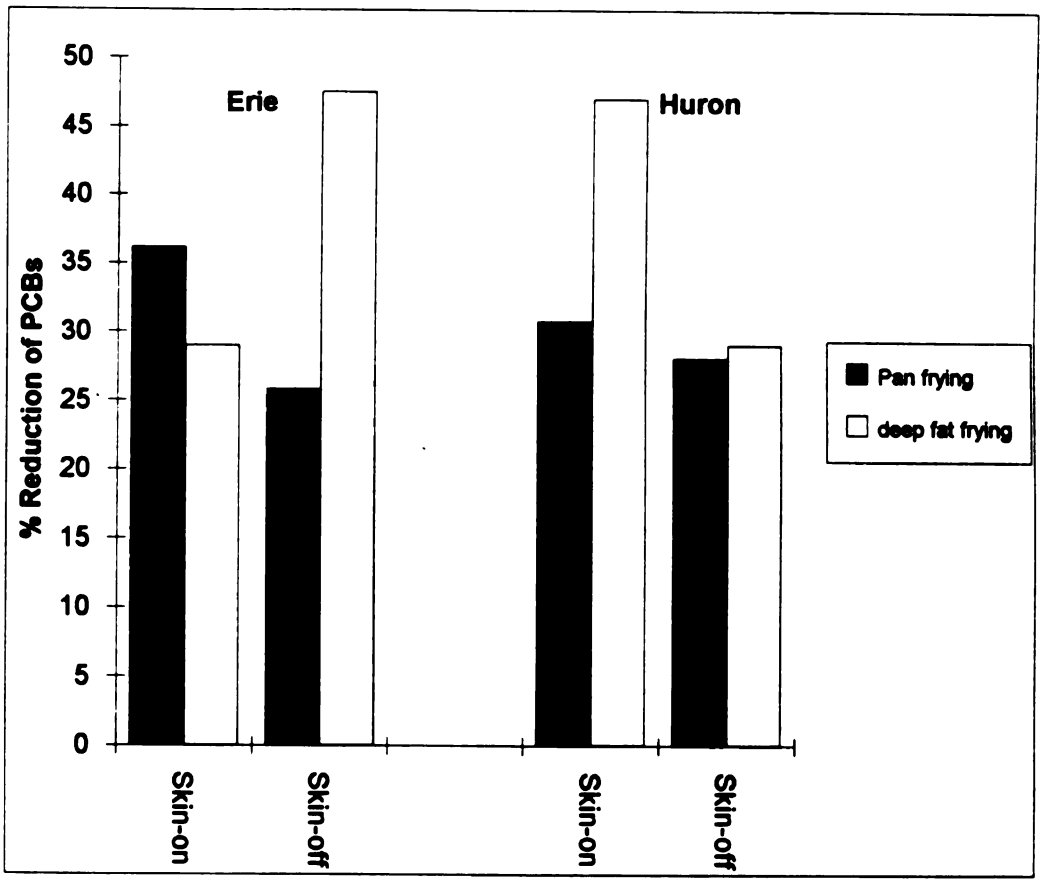
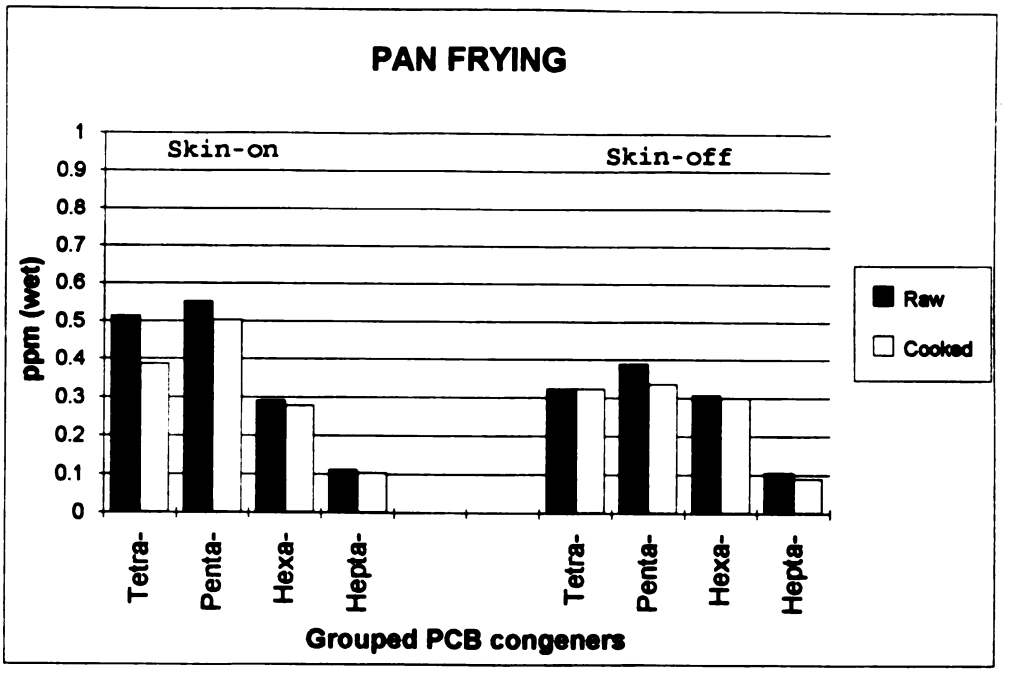


Figure 10. The percent reduction of total PCB congeners by pan frying and deep fat frying

Cooking Effects on The Reduction of PCB Homolog Congeners and Specific Congeners

The most potent PCB congeners are some of the congeners most resistant to degradation and metabolism and may be selectively enriched, relative to other PCB congeners (Tenabe et al., 1987). Since most of the threatening congeners are tetra-, penta-, hexa-, and hepta- congeners based on their abundance and potential toxicity, the concerning was focused on those congeners. The game fish and selected bottom feeders were analyzed at EPA (1992) to indicate the potential for risk to human health from fish consumption. In the EPA research entitled "National Study of Chemical Residues in Fish", concentration of hexachloro-biphenyls was highest, followed by pentachlorobiphenyls (hexa- > penta- > tetra- > heptachlorobiphenyls). The cooking effects on those homolog congeners and distribution pattern of this research are shown in Figures 11 and 12 and the actual means and standard deviations are presented in Tables 12 and 13. And since both fat and moisture are lost during cooking, expression based on micrograms per fillet which considered weight loss during cooking are also presented in Figures 11 and 12 which refract actual change during cooking. The levels of each PCB homolog congeners were reduced by both pan frying and deep fat frying.



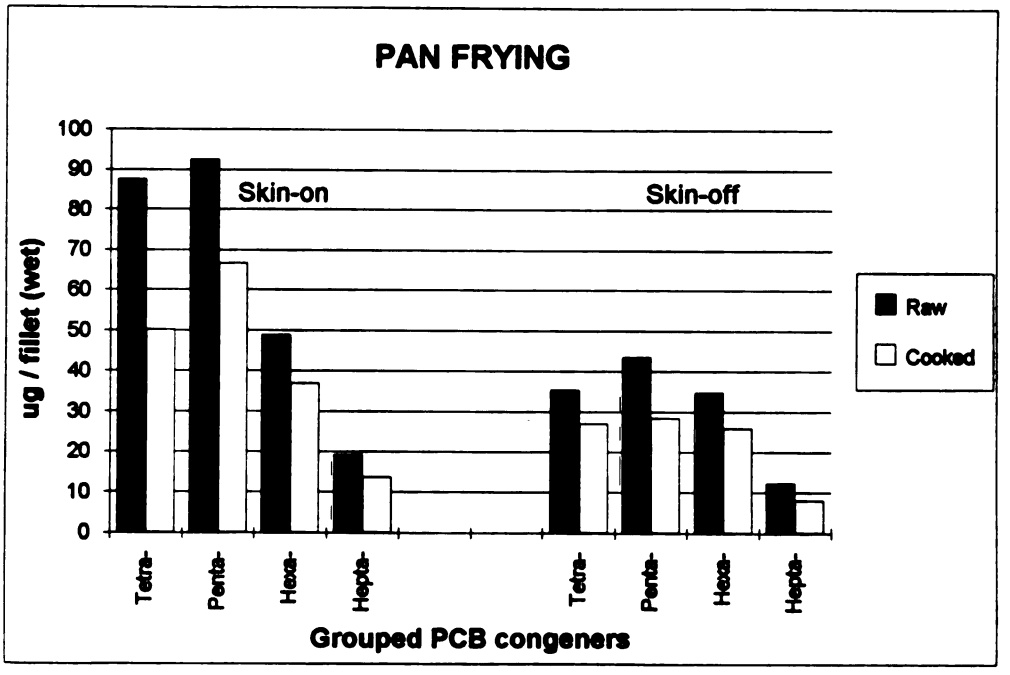
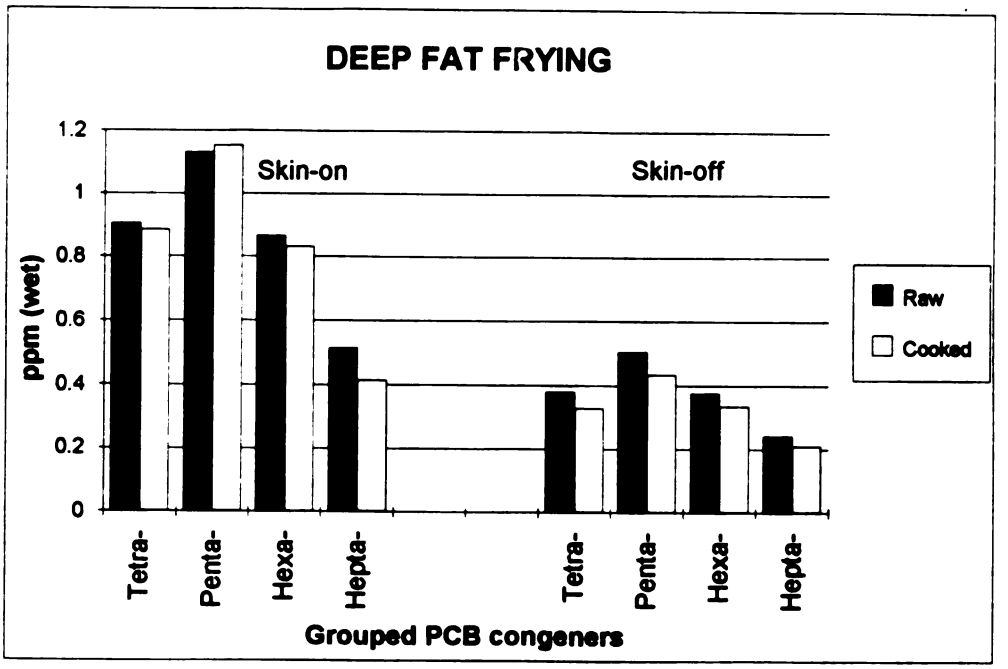


Figure 11-a. Each grouped PCB congeners in raw and pan fried carp harvested from Lake Erie.



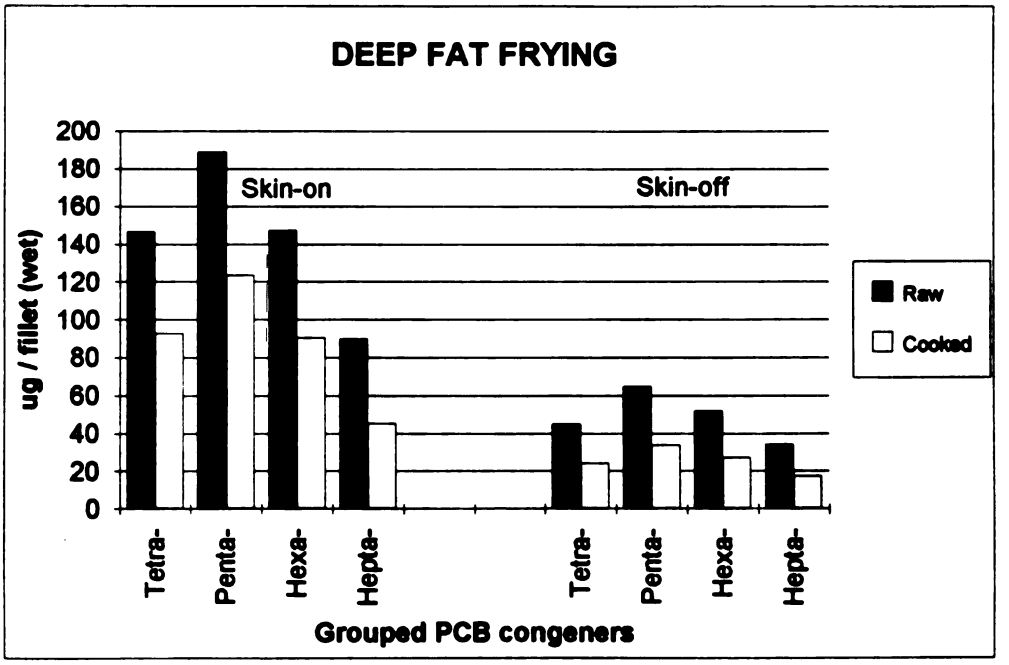
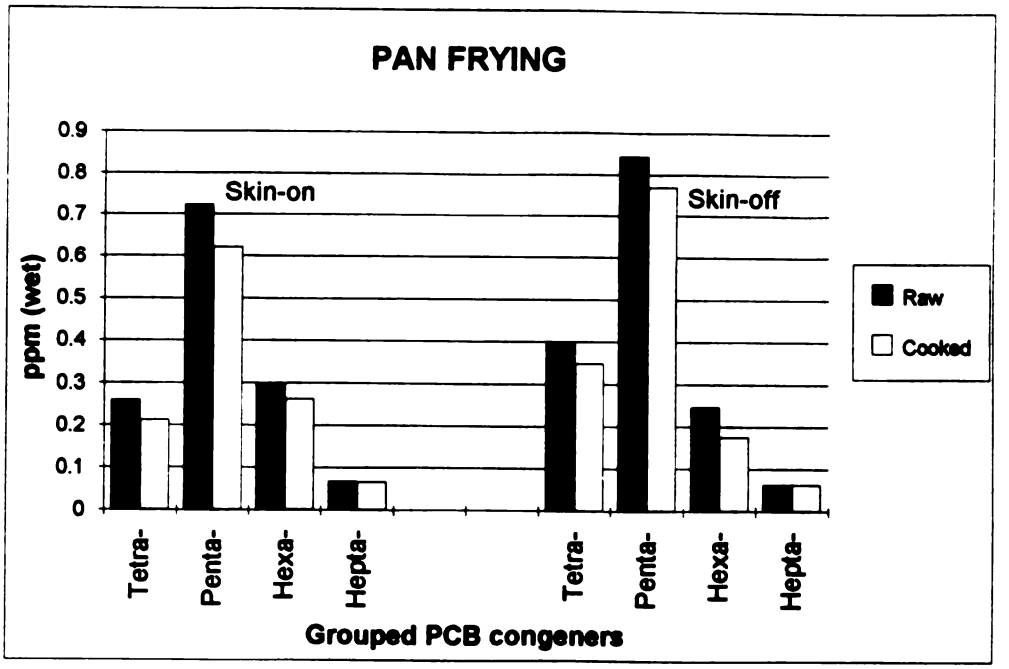


Figure 11-b Each grouped PCB congeners in raw and deep fat fried carp harvested from Lake Erie.



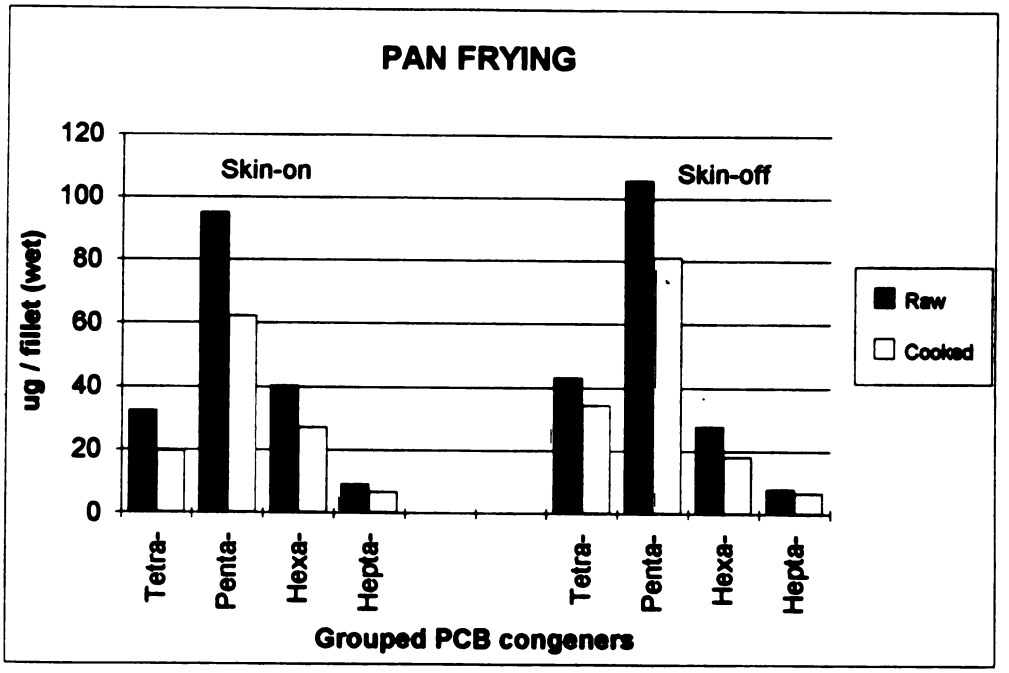
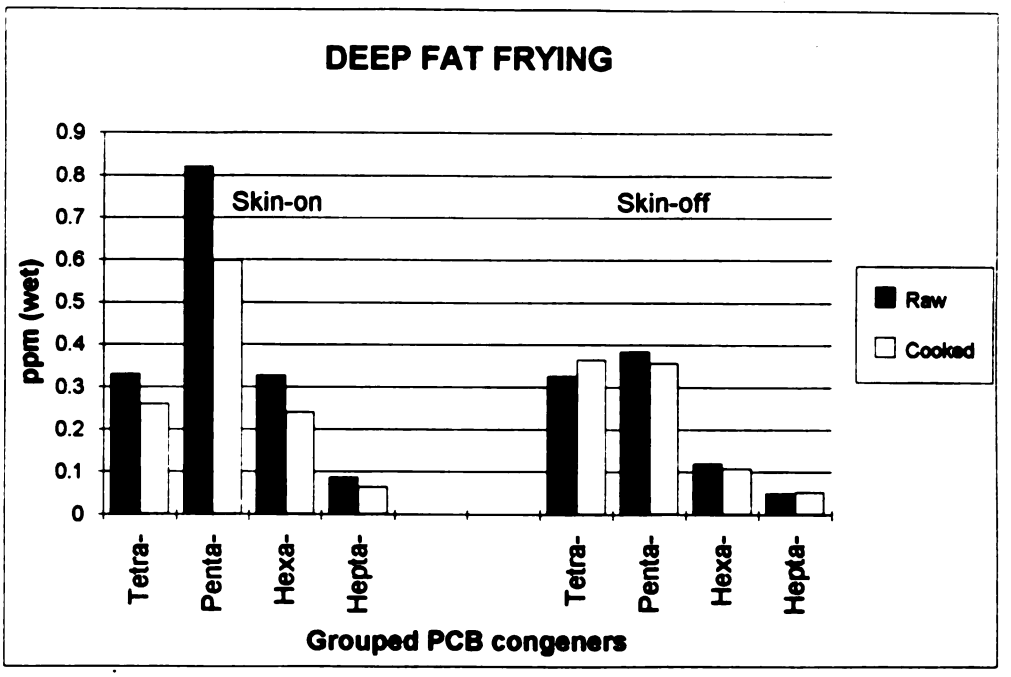


Figure 12-a. Each grouped PCB congeners in raw and pan fried carp harvested from Lake Huron.



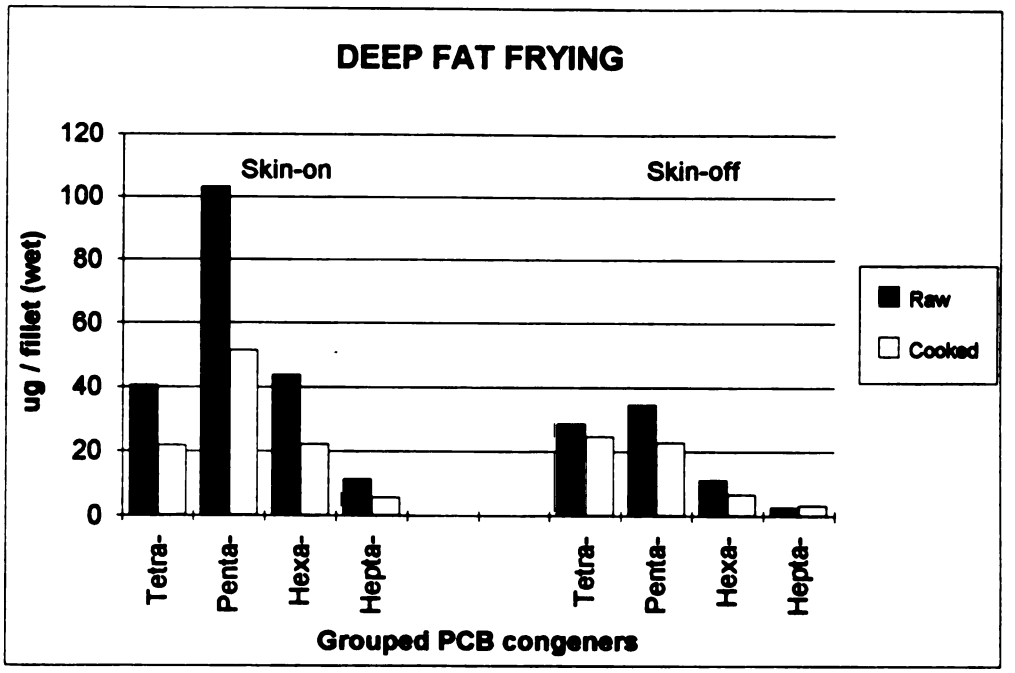


Figure 12-b. Each grouped PCB congeners in raw and deep fat fried carp harvested from Lake Huron

Table 12-a. PCB homolog congeners expressed as ppm wet tissue in raw and cooked carp fillets harvested from Lake Erie

Cooking Method	Skin	Homolog	PCB Content (ppm) Raw	Cooked
Pan Frying	Skin-on	Tri-	0.032±0.019	0.024±0.021
		Tetra-	0.513±0.253	0.388±0.246
		Penta-	0.552±0.230	0.503±0.305
		Hexa-	0.291±0.204	0.279±0.251
		Hepta-	0.112±0.083	0.103±0.113
		Octa-	0.022±0.010	0.019±0.014
	Skin-off	Tri-	0.022±0.012	0.020±0.014
		Tetra-	0.324±0.108	0.323±0.138
		Penta-	0.390±0.137	0.337±0.095
		Hexa-	0.307±0.148	0.300±0.134
		Hepta-	0.105±0.081	0.090±0.044
		Octa-	0.016±0.009	0.023±0.024
Deep Fat Frying	Skin-on	Tri-	0.073±0.053	0.070±0.047
		Tetra-	0.904±0.327	0.884±0.182
		Penta-	1.131±0.643	1.152±0.390
		Hexa-	0.864±0.621	0.831±0.421
		Hepta-	0.515±0.516	0.413±0.342
		Octa-	0.060±0.054	0.063±0.034
	Skin-off	Tri-	0.045±0.037	0.025±0.012
		Tetra-	0.379±0.142	0.328±0.146
		Penta-	0.505±0.315	0.433±0.288
		Hexa-	0.376±0.389	0.333±0.353
		Hepta-	0.240±0.325	0.209±0.285
		Octa-	0.023±0.027	0.022±0.027

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

Table 12-b. PCB homolog congeners expressed as micrograms per fillet in wet tissue of raw and cooked carp harvested from Lake Erie

Cooking Method	Skin	Homolog	PCB Content (ug/fillet) Raw	Cooked
Pan Frying	Skin-on	Tri-	5.43±3.32	3.10±2.77
		Tetra-	87.57±49.78	50.06±31.73
		Penta-	92.39±44.98	66.67±45.38
		Hexa-	48.94±39.24	36.99±36.56
		Hepta-	19.11±16.47	13.63±16.34
		Octa-	3.75±2.18	2.47±2.16
	Skin-off	Tri-	2.27±0.94	1.63±0.78
		Tetra-	35.34±11.36	27.07±10.32
		Penta-	43.59±19.15	28.50±7.29
		Hexa-	34.67±20.90	25.98±13.52
		Hepta-	12.25±10.80	7.97±4.45
		Octa-	1.81±1.22	2.06±2.30
Deep Fat Frying	Skin-on	Tri-	11.74±8.33	7.33±4.49
		Tetra-	146.60±70.96	92.52±23.97
		Penta-	189.05±139.32	123.40±55.08
		Hexa-	147.33±130.10	90.47±55.50
		Hepta-	89.78±102.93	45.23±39.02
		Octa-	10.33±10.86	6.91±4.55
	Skin-off	Tri-	5.03±3.52	1.91±1.29
		Tetra-	44.93±26.24	24.11±14.04
		Penta-	64.72±63.33	33.75±31.35
		Hexa-	51.78±72.76	27.26±37.20
		Hepta-	34.20±58.16	17.50±29.32
		Octa-	3.12±4.94	1.79±2.75

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

Table 13-a. PCB homolog congeners expressed as ppm wet tissue in raw and cooked carp fillets harvested from Lake Huron

Cooking Method	Skin	Homolog	PCB Content (ppm) Raw	Cooked
Pan Frying	Skin-on	Tri-	0.022±0.009	0.023±0.011
		Tetra-	0.259±0.108	0.211±0.100
		Penta-	0.722±0.506	0.622±0.484
		Hexa-	0.297±0.227	0.262±0.214
		Hepta-	0.067±0.054	0.066±0.043
		Octa-	0.027±0.029	0.024±0.025
	Skin-off	Tri-	0.036±0.027	0.030±0.030
		Tetra-	0.395±0.449	0.349±0.450
		Penta-	0.843±1.349	0.769±1.154
		Hexa-	0.246±0.271	0.175±0.243
		Hepta-	0.063±0.094	0.063±0.098
		Octa-	0.008±0.006	0.009±0.007
Deep Fat Frying	Skin-on	Tri-	0.030±0.021	0.021±0.013
		Tetra-	0.329±0.170	0.259±0.114
		Penta-	0.821±0.459	0.599±0.343
		Hexa-	0.326±0.275	0.240±0.221
		Hepta-	0.086±0.057	0.064±0.043
		Octa-	0.006±0.004	0.005±0.002
	Skin-off	Tri-	0.017±0.012	0.019±0.014
		Tetra-	0.325±0.179	0.364±0.249
		Penta-	0.383±0.115	0.356±0.126
		Hexa-	0.120±0.050	0.108±0.035
		Hepta-	0.049±0.020	0.052±0.031
		Octa-	0.004±0.002	0.006±0.001

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

Table 13-b. PCB homolog congeners expressed as micrograms per fillet in wet tissue of raw and cooked carp harvested from Lake Huron

			PCB Content (ug/fillet)	
Cooking Method	Skin	Homolog	Raw	Cooked
Pan Frying	Skin-on	Tri-	2.22±0.93	1.92±0.87
		Tetra-	32.34±23.43	19.40±12.46
		Penta-	95.02±93.04	62.32±60.91
		Hexa-	40.31±41.92	27.12±27.14
		Hepta-	9.20±9.95	6.72±5.80
		Octa-	4.02±5.06	2.48±3.07
	Skin-off	Tri-	3.36±3.89	2.60±3.69
		Tetra-	43.24±73.36	34.35±62.59
		Penta-	105.80±212.56	81.14±156.95
		Hexa-	27.76±39.38	18.13±33.23
		Hepta-	7.86±14.94	6.75±13.21
		Octa-	0.76±0.91	0.74±0.82
Deep Fat Frying	Skin-on	Tri-	3.15±2.24	1.62±1.22
		Tetra-	40.50±28.94	21.76±14.37
		Penta-	103.17±80.46	51.36±42.13
		Hexa-	43.80±44.54	22.11±25.00
		Hepta-	11.30±9.72	5.66±5.04
		Octa-	0.77±0.60	0.46±0.32
	Skin-off	Tri-	1.41±1.25	1.22±1.38
		Tetra-	28.59±26.48	24.61±30.29
		Penta-	34.58±27.72	22.62±19.49
		Hexa-	11.10±10.35	6.74±5.15
		Hepta-	4.41±3.86	3.18±2.37
		Octa-	0.42±0.38	0.36±0.29

n = 6
Pan fried samples: only muscle tissue analyzed.
Deep fat fried samples: included skin.

However, it is not surprising that the deep fat fried, skin-on fillets had higher levels of each homologs and total PCBs than did the pan fried fish because deep fat fried, skin-on fish were analyzed with skin. The levels of those grouped PCB congeners existed in both raw and cooked fish fillets with same patterns of distribution (penta- > tetra- > hexa- > heptachlorobiphenyls), with only a little exception. Even though it was not consistent to EPA's report, the penta-PCB congeners might show a high level due to accumulation and abundance in environment. The distribution pattern may be affected by the difference in chlorine contents of various PCBs in an aquatic environment. However, it did not have a specific relationship between the reduction of PCBs during cooking and the number of chlorines in PCBs. The percentage reductions of each PCB homolog by cooking are shown in Figures 13 and 14.

The pattern of specific PCB congener distribution in raw and pan fried and deep fat fried carp fillets from Lake Erie and Huron are shown in Figures 15 through 18, respectively. The values which are expressed as ppm wet tissue do not take into account the weight loss during the deep fat frying or pan frying. In contrast, the values expressed as micrograms per fillet do show loss during cooking. The specific PCB congener values in the cooked fillets were generally lower than in the raw.

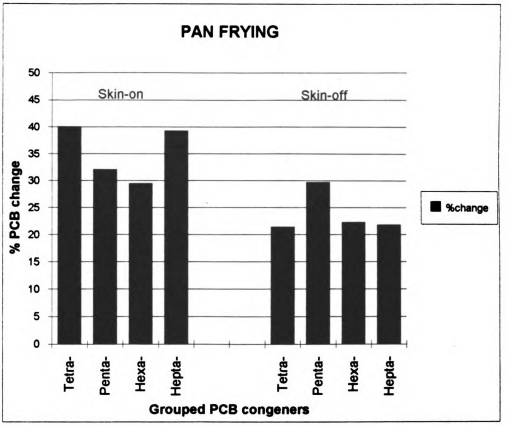


Figure 13-a. Percentage reduction of each grouped PCB congeners by pan frying carp harvested from Lake Erie (Skin-on pan fried sample had only muscle tissue)

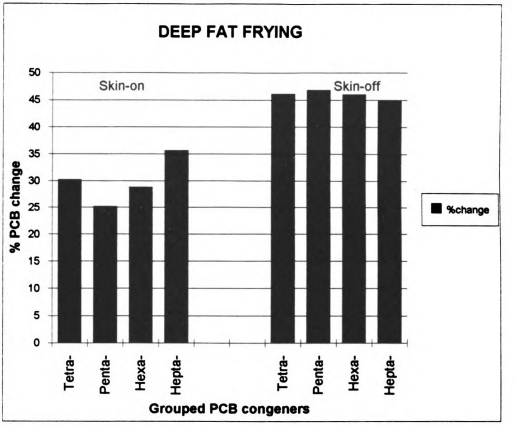


Figure 13-b. Percentage reduction of each grouped PCB congeners by deep fat frying carp harvested from Lake Erie (Skin-on deep fat fried sample included skin)

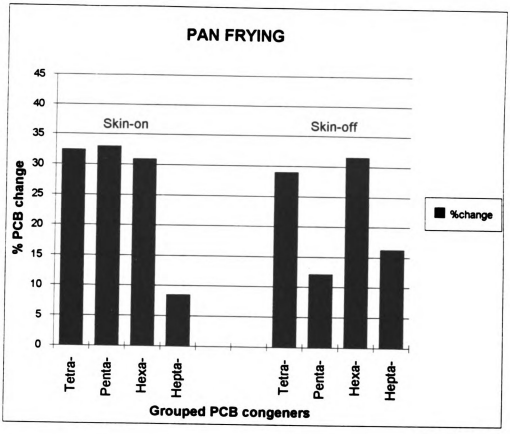


Figure 14-a. Percentage reduction of each grouped PCB congeners by pan frying carp harvested from Lake Huron (Skin-on pan fried sample had only muscle tissue)

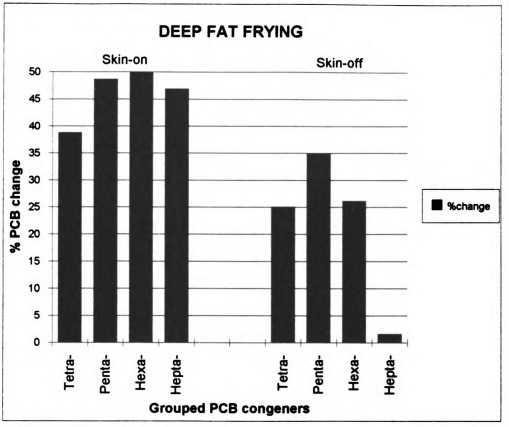
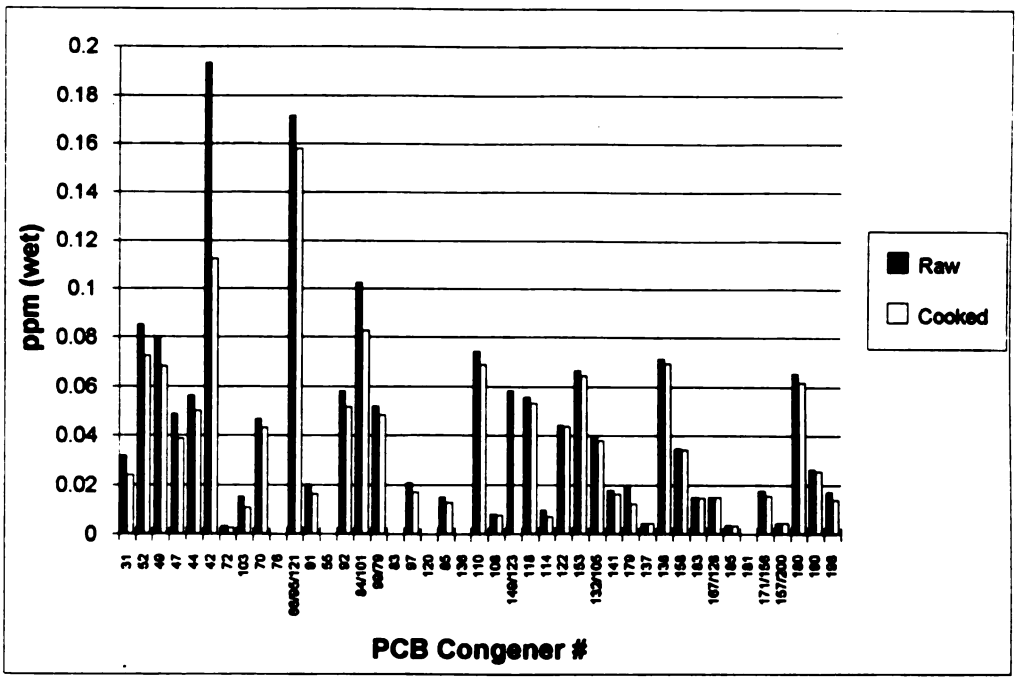


Figure 14-b. Percentage reduction of each grouped PCB congeners by deep fat frying carp harvested from Lake Huron (Skin-on deep fat fried sample included skin)



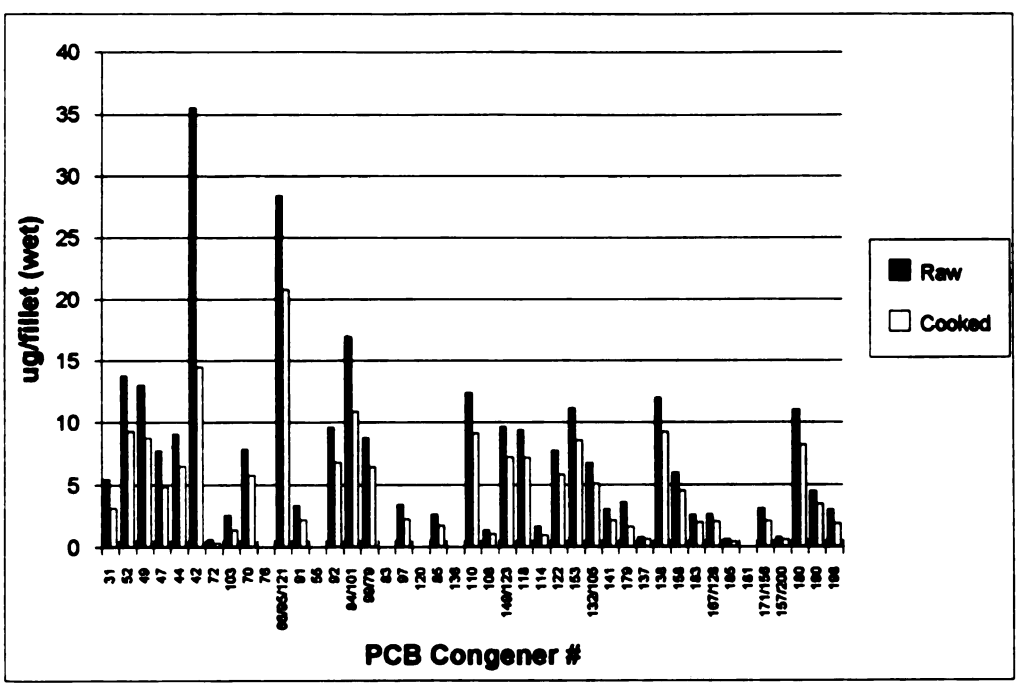
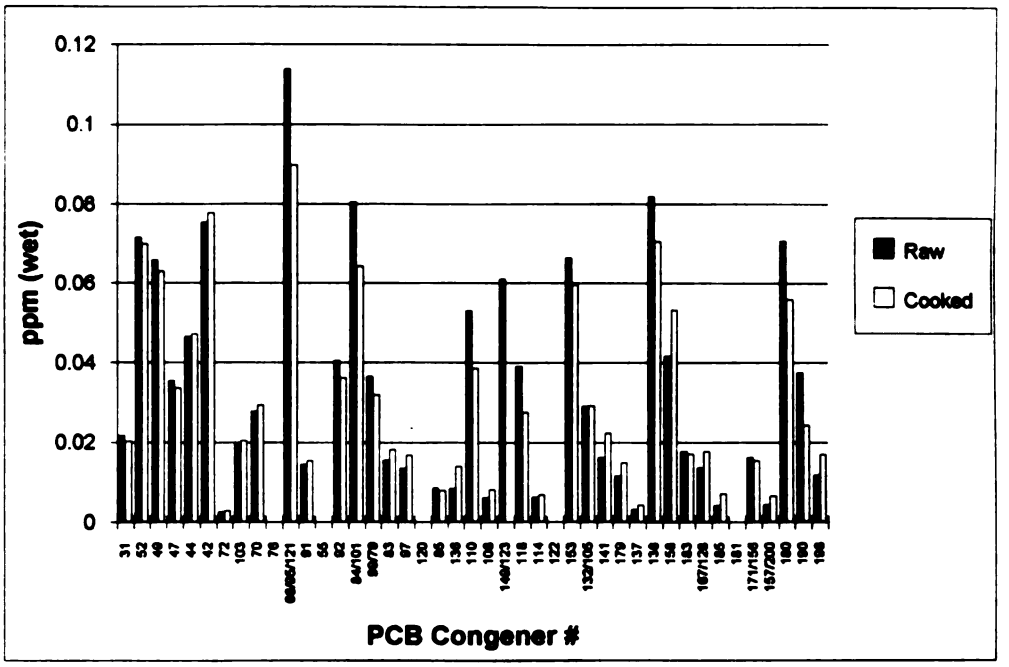


Figure 15-a. Congener specific PCBs in raw and pan fried carp from Lake Erie, skin-on.



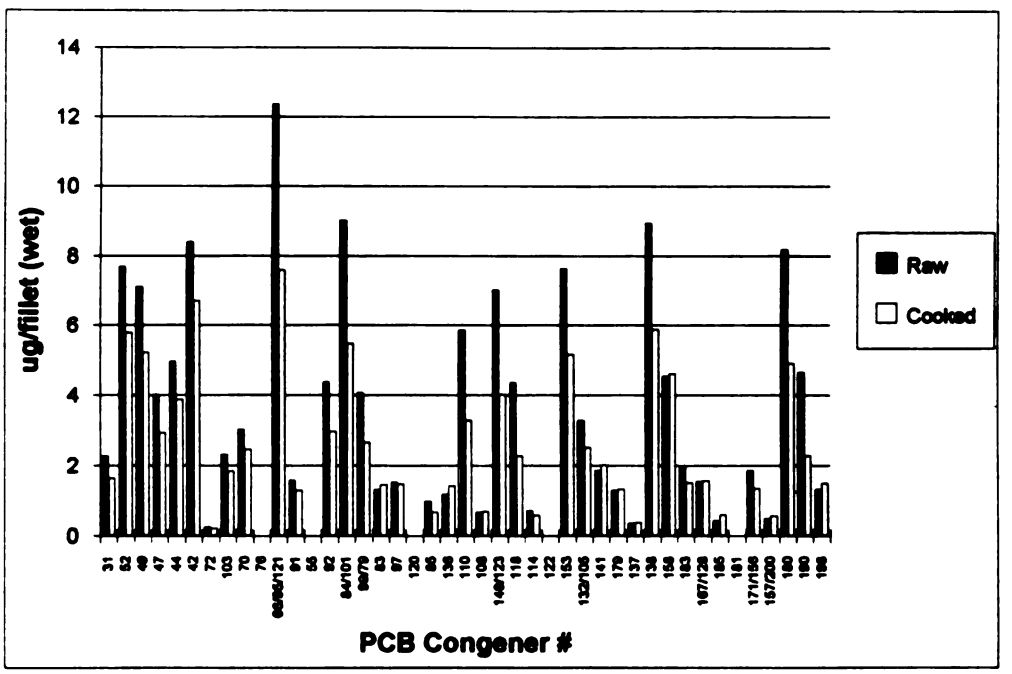


Figure 15-b. Congener specific PCBs in raw and pan fried carp from Lake Erie, skin-off.

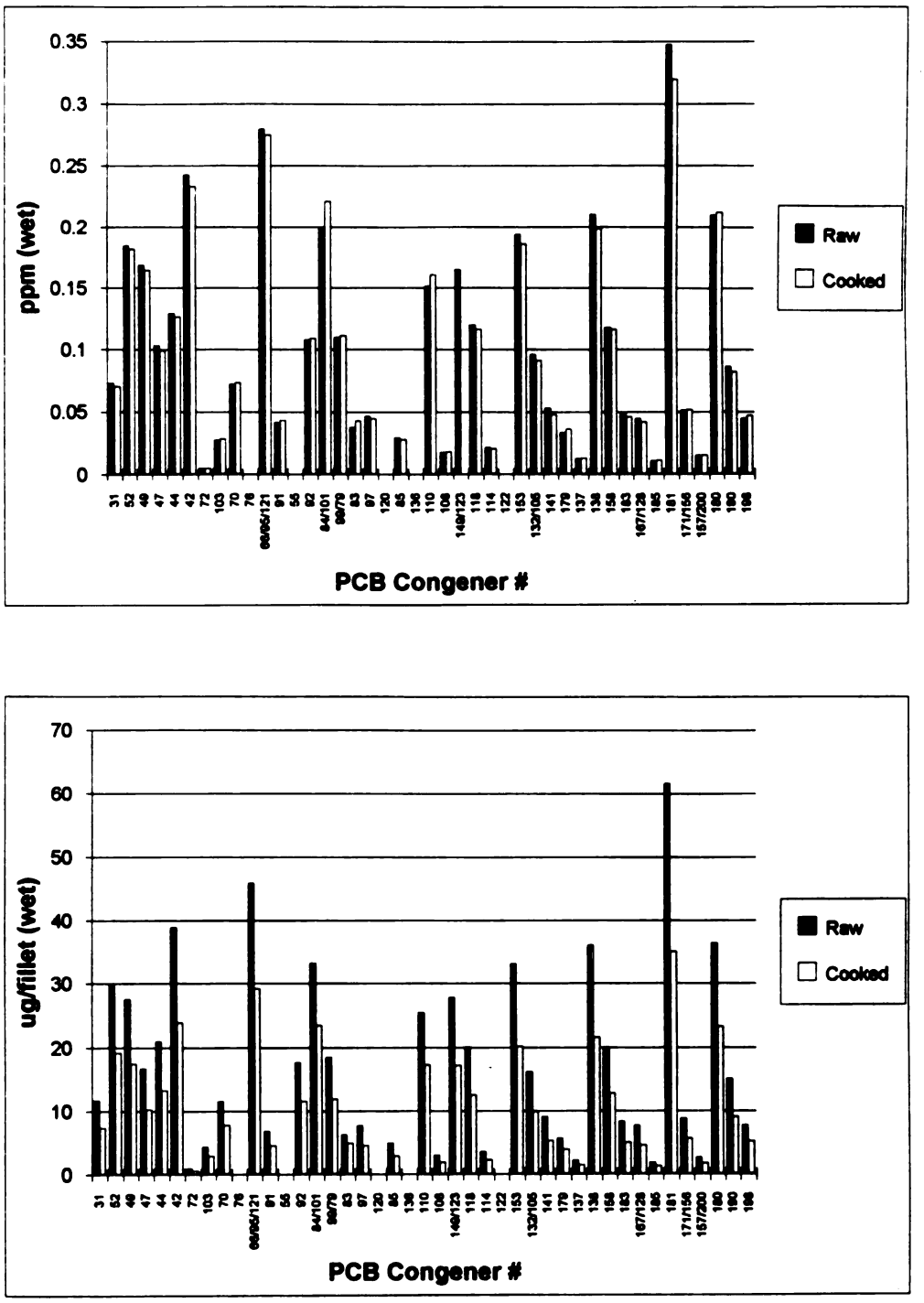
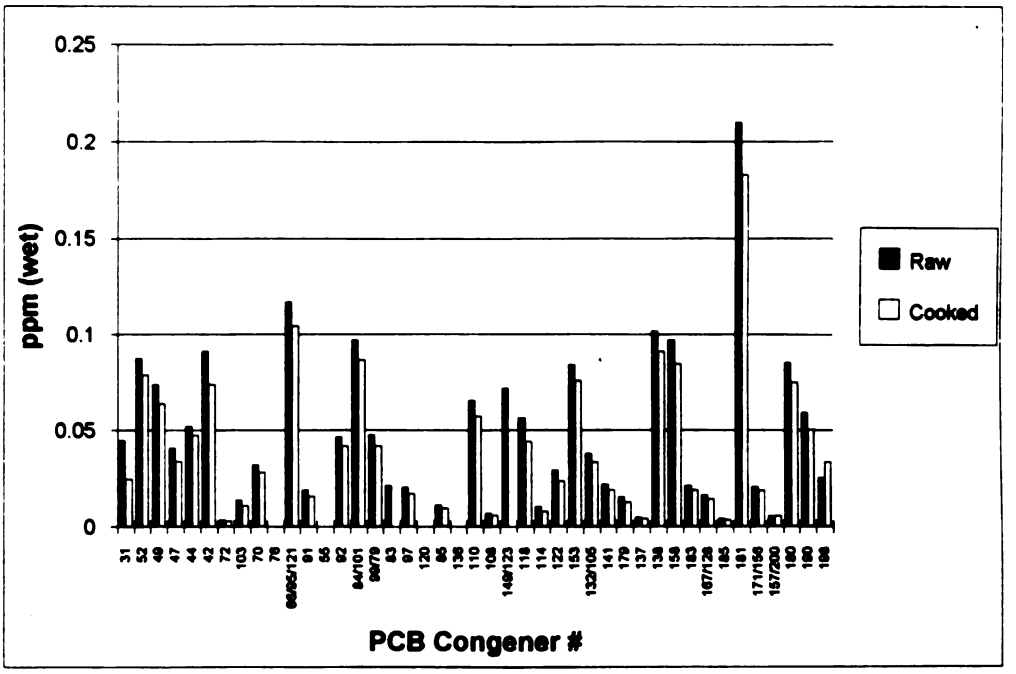


Figure 16-a. Congener specific PCBs in raw and deep fat fried carp from Lake Erie, skin-on.



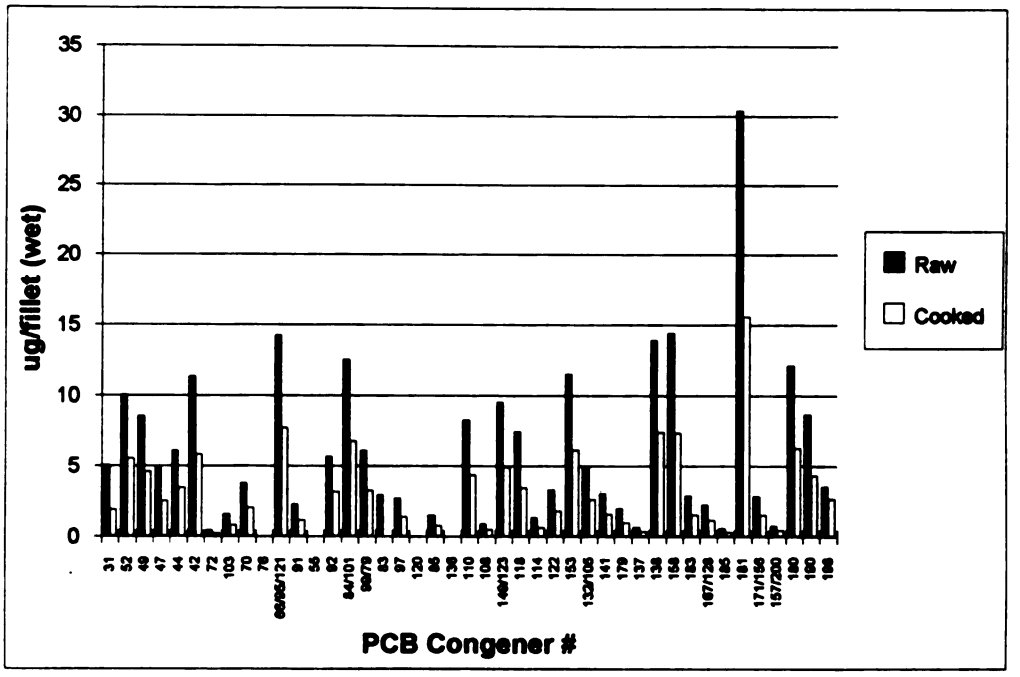
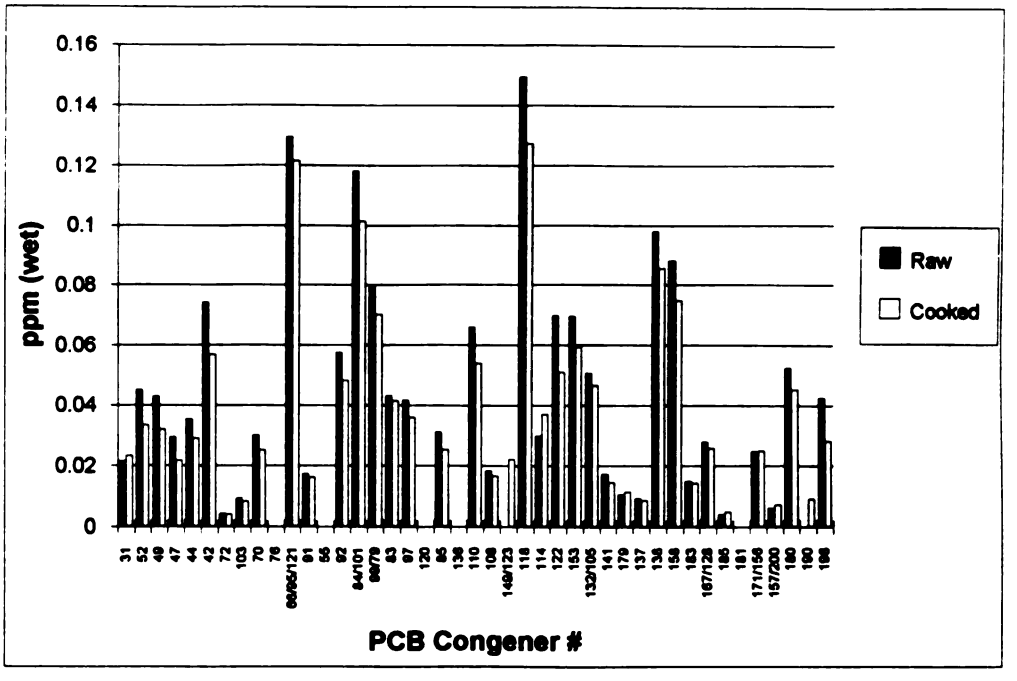


Figure 16-b. Congener specific PCBs in raw and deep fat fried carp from Lake Erie, skin-off.



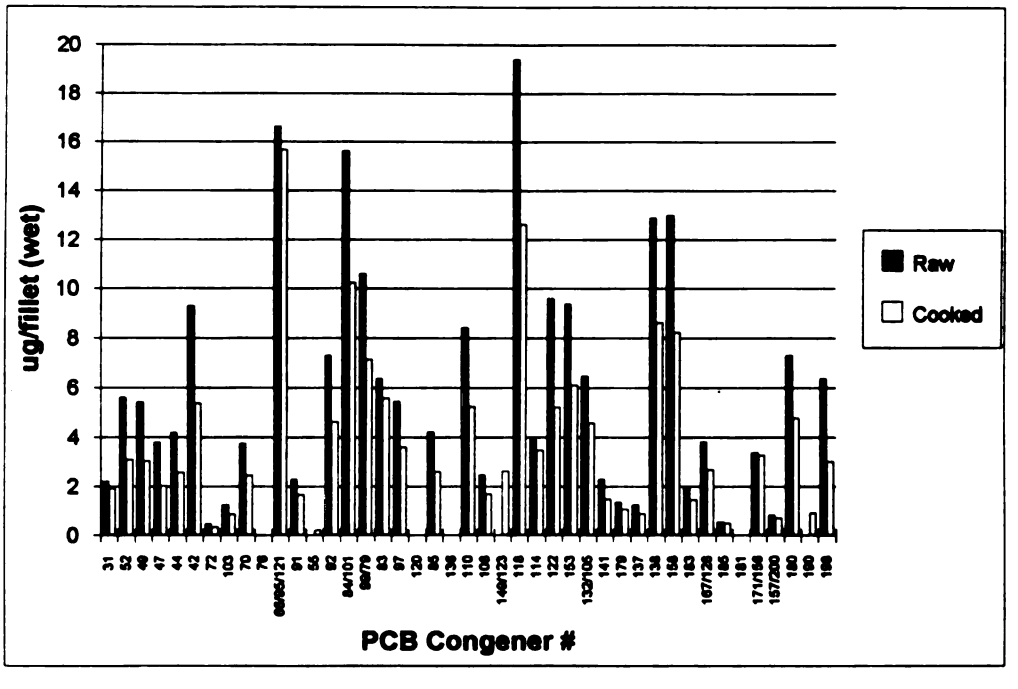
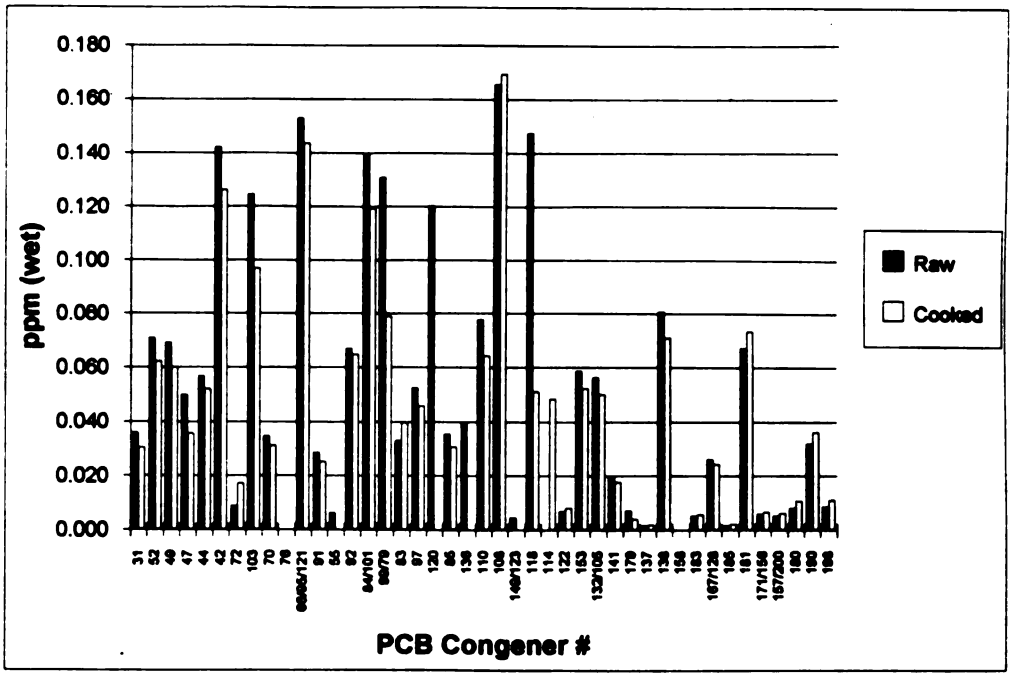


Figure 17-a. Congener specific PCBs in raw and pan fried carp from Lake Huron, skin-on.



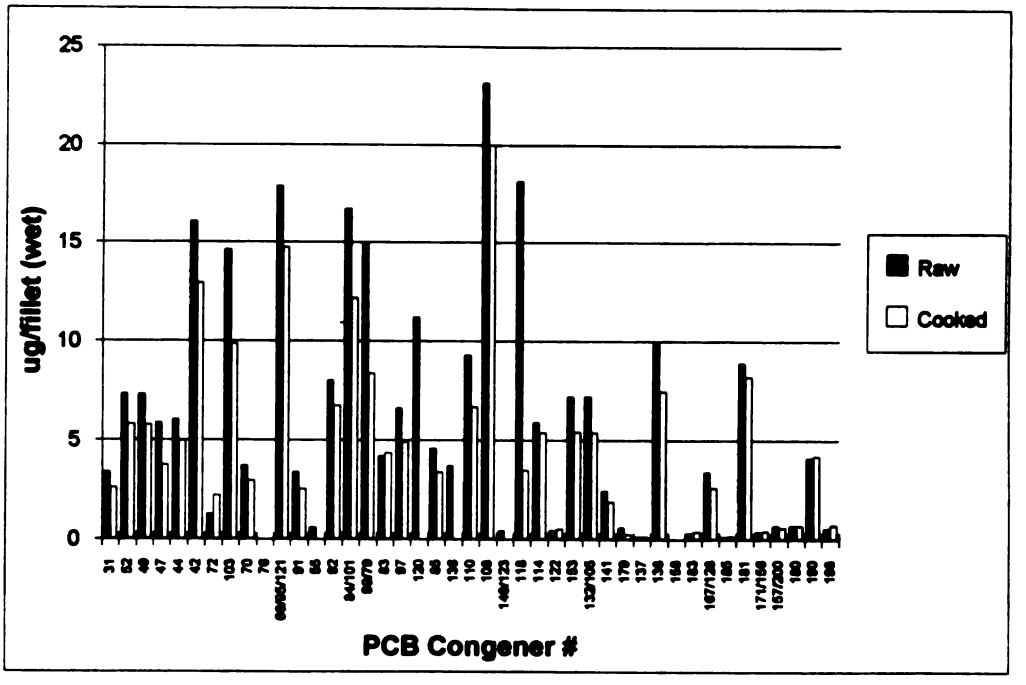
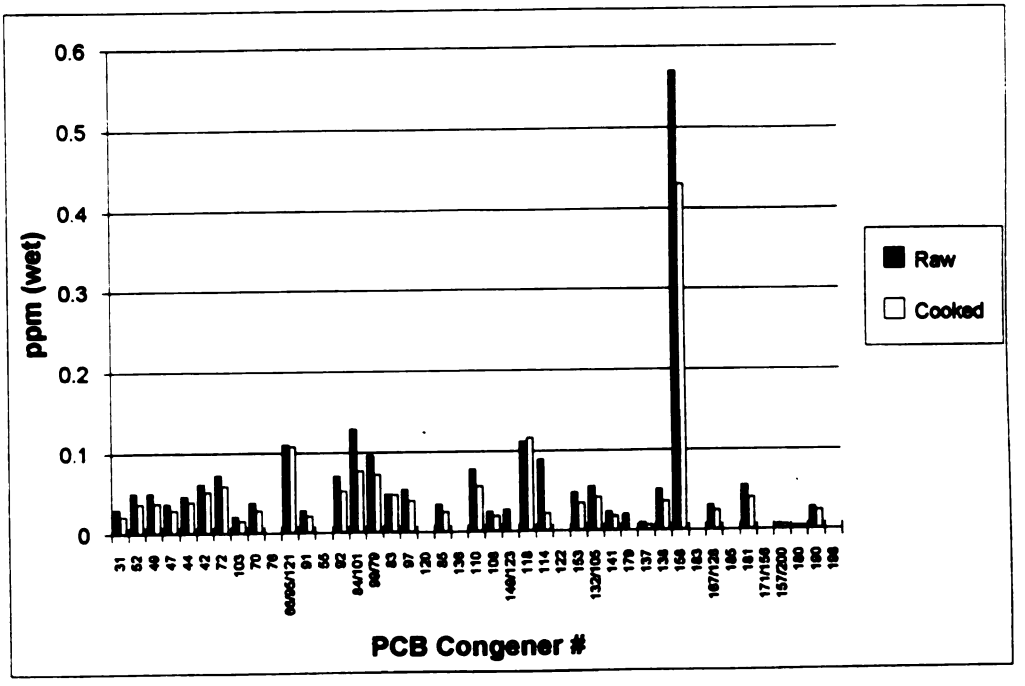


Figure 17-b. Congener specific PCBs in raw and pan fried carp from Lake Huron, skin-off.



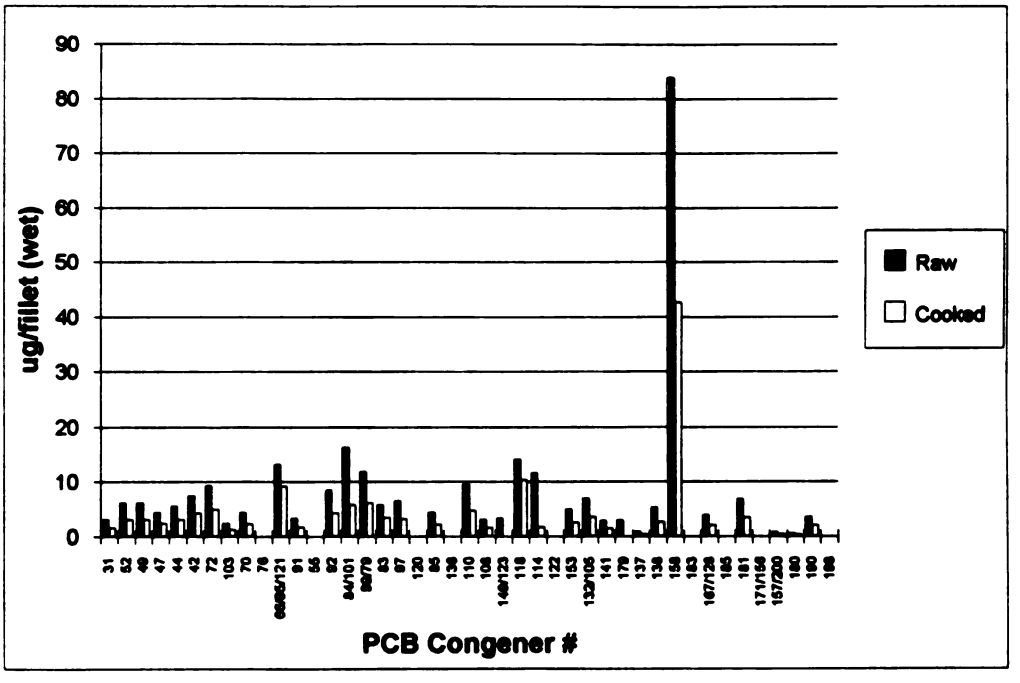
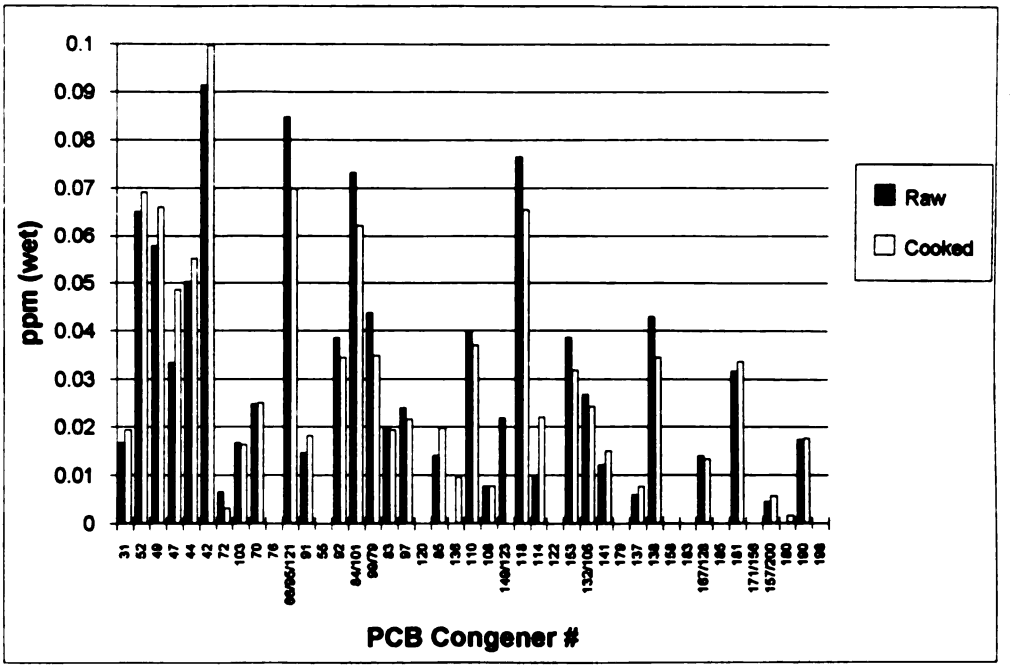


Figure 18-a. Congener specific PCBs in raw and deep fat fried carp from Lake Huron, skin-on.



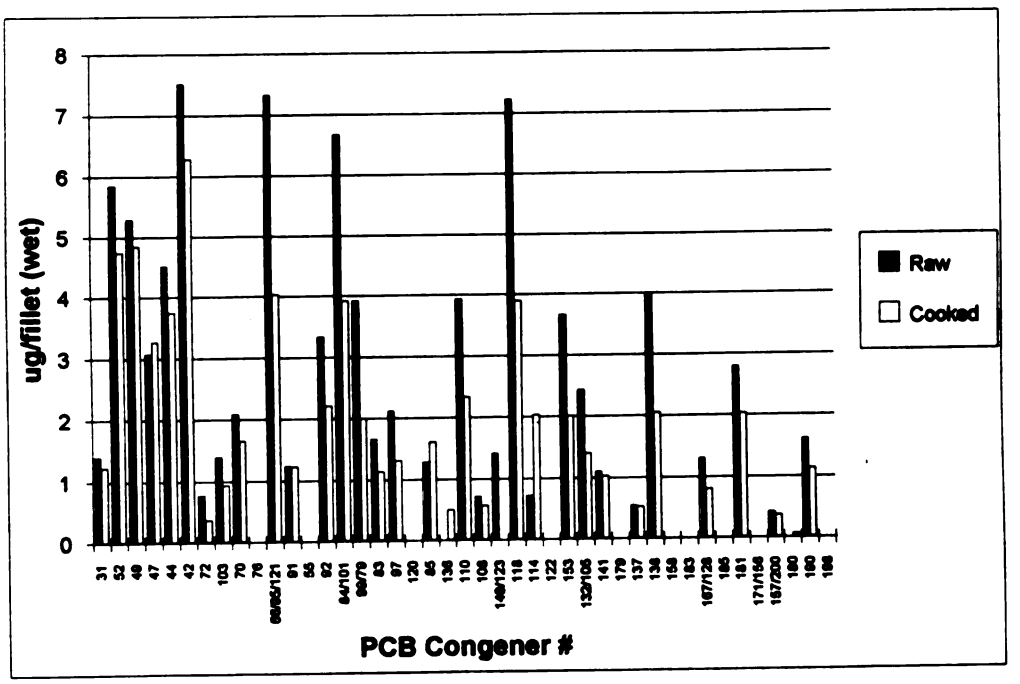


Figure 18-b. Congener specific PCBs in raw and deep fat fried carp from Lake Huron, skin-off.

Skin-on carp fillets which were deep fat fried were analyzed with skin since deep fat fried fish are usually ingested with skin by consumers. Only the muscle tissue of the pan fried skin-on carp fillets was used for the cooked carp analyses. Thus, it is difficult to compare the percent change of PCBs during cooking. It was likely that the percent reductions by deep fat frying skin-on carp would be lower than those by pan frying. However, it is suprising that deep fat fried skin-on carp harvested from Lake Huron (Figure 14-b) lost greater percent of PCBs than pan fried skin-on carp (Figure 14-a).

Skin Removal Effects on PCBs Reduction

Any food process which removes lipid from fish may alter the PCB levels in the fish. The removal of skin and its associated fat from fish reduced the specific congeners, homologs and total PCBs as expected. The removal of skin and its associated fat from fish per se reduced the total PCBs level. Skin-on carp fillets had significantly greater values of PCBs than skin-off carp as shown in Figure 19. The differences for skin-on and skin-off carp are illustrated by the following average group values expressed as ppm wet tissue:

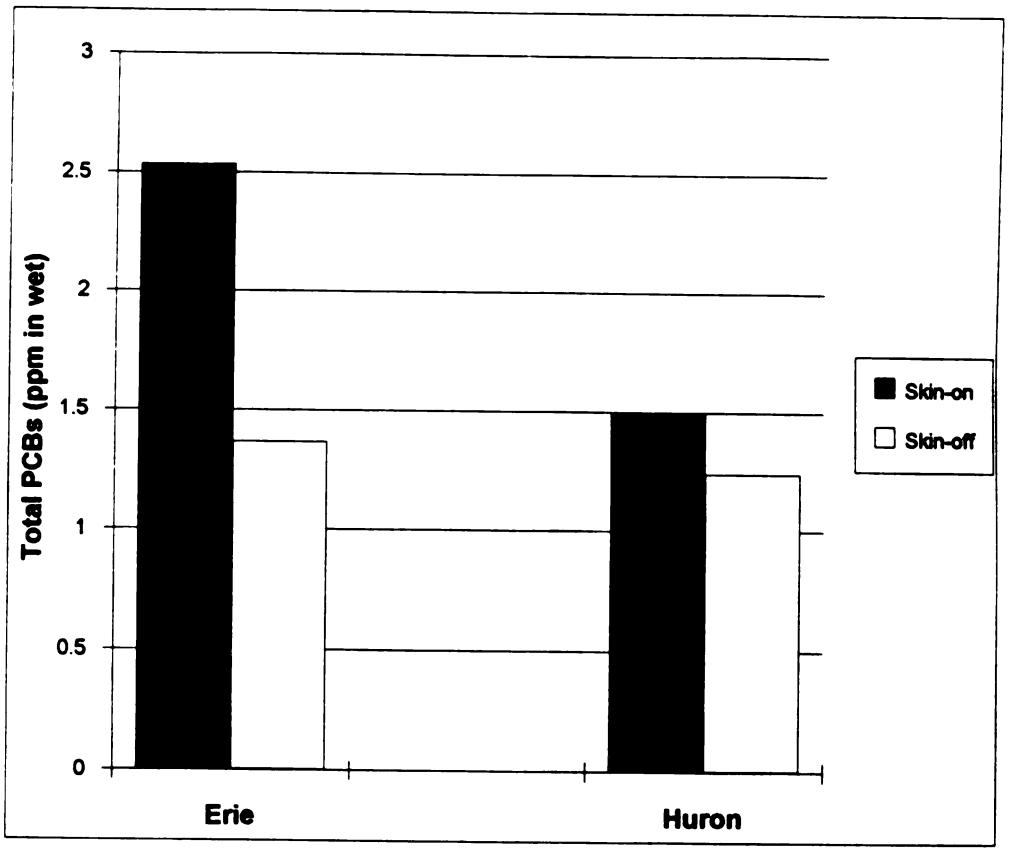


Figure 19. The average total PCBs in skin-on and skin-off carp from Lake Erie and Lake Huron.

Group	Skin-on		Skin-off
Tri-	0.037	>	0.026
Tetra-	0.469	>	0.349
Penta-	0.763	>	0.502
Hexa-	0.424	>	0.246
Hepta-	0.178	>	0.109
Octa-	0.028	>	0.013
Total PCBs	1.898	>	1.244

The Packed column GC analyses by Michigan Department of Public Health (Zabik et al., 1993) also determined the level of total PCBs in skin-on carp was higher than skin-off carp. The reduction of PCB levels in fish fillets through removal of skin was also determined by Zabik et al. (1979), Hora (1981) and Sanders and Haynes (1988). Since PCBs are lipid-soluble, some of the PCBs are dissolved in fat portion. Yoshida et al. (1973) observed the high levels of PCBs in the skin and dark muscle of carp. Therefore, it is recommended to remove the skin, fatty areas under skin, lateral line, dorsal fat, and belly flap before consuming, since all of these parts tend to have higher levels of PCBs and other chlorinated pesticides. The presence or absence of skin significantly affected the total PCBs and specific congener levels in fish fillets themselves (Appendix 6-6,

6-8). However skinning did not affect the effectiveness in reducing PCBs during cooking (Appendix 6-9).

The PCBs, lipophilic contaminants may pose a threat to the health of consumers by contaminated fish from lakes. Even though State and Federal agencies have monitored environmental contaminants, consumers should try to reduce the contaminants in food. Therefore, they are encouraged to skin carp fillets before cooking.

CONCLUSION

One of the most frequently noted differences in health between fishing villagers and people in industrialized areas is the low incidence of heart attacks and other major diseases. The consumption of fish products can be related to such a low incidence (Lands, 1986). The Great Lakes are important in providing fresh water fish to people living inland. However the consumption of Great Lakes fish provides a PCB exposure to fish eaters. PCBs are no longer manufactured but they continue to be found in fish from the Great Lakes. PCBs may pose a health threat to fish consumers. These PCBs and other contaminants in fish from Great Lakes have resulted in a hesitation of fish, especially sport fish consumption.

This study in which congener specific PCBs were analyzed by capillary column gas chromatography, has demonstrated that the average level of total PCBs based on summing individual congeners commonly found in Aroclor® 1254 was 2.534 ppm in skin-on carp, 1.367 ppm in skin-off carp from Lake Erie and 1.496 ppm in skin-on carp, 1.240 ppm in skin-off carp from Lake Huron. The packed column analyses

at the Michigan Department of Public Health (Zabik et al., 1993) also showed the higher values in the carp harvested from Lake Erie. The average level of total PCBs in carp from Lake Erie was higher than those from Lake Huron, which might be partly due to larger size of carp from Lake Erie. Four of six carp from Lake Erie exceeded 2 ppm which is the FDA's tolerance level of PCBs for fish.

The effects of pan frying and deep fat frying on reduction of total PCBs and PCB homolog congeners were also determined. Cooked samples showed the lower levels of PCBs than uncooked samples, in contrast to previous PCBs study in carp (Zabik et al., 1982), even though the average fat content in carp was relatively low. However the statistical comparison between two cooking methods showed no significant difference for the effectiveness in reducing PCB levels, even though deep fat frying was a little more effective than pan frying. The average percent reduction of total PCBs based on total micrograms per fillet was 30.2±14.1% by pan frying, 38.1±15.6% by deep fat frying.

Since most of the threatening congeners are tetra-, penta-, hexa-, and heptachlorobiphenyls based on their abundance and potential toxicity, the distribution of PCBs in carp and cooking effect on those PCB congeners were determined in this study. In both raw and cooked carp, the distribution of each PCB homolog congeners was in order;

penta- > tetra- > hexa- > heptachlorobiphenyls. However the distribution of PCB homolog congeners in EPA study (1992) was in order: hexa- > penta- > tetra- > hepta homolog. Even though they were not consistent with each other, it is thought that the penta homolog showed a high level due to accumulation and abundance in environment, and low level of hepta homolog due to low abundance in environment. And it did not show the special relationship between the reduction of PCBs during cooking and the number of chlorines in PCBs.

The average total PCB level in skin-off carp were lower than skin-on carp. Since PCBs are lipid-soluble and dissolved in fat portions of fish, it is possible to remove some of PCBs. Skin and fat removal did not significantly affect the cooking effectiveness in reducing PCBs in carp.

The States and Federal agencies have monitored and regulated the level of PCBs in fish that commercially marketed. Therefore sports fishermen or subsistence fishermen need to be more careful and try to reduce the PCBs and other contaminants in fish. Cooking and appropriate processing can be an additional safety factor. Skin and fatty area under skin, the lateral line, belly flap should be removed before consuming fish.

In addition to PCBs, many Great Lakes fish contain other toxic compounds, including pesticides such as DDT, dieldrin, chlordane, mirex, and toxaphene. They also contain

mercury. Therefore, fish consumption advisories and public education should provide information to reduce the health risk from contaminated fish.

PROPOSALS FOR FUTURE RESEARCH

This study had considered the level of total PCBs, the grouped homolog congeners, and some specific PCB congeners based on Aroclor® 1254. However the majority of PCBs apparently have no effect on mammalian system (McKinney and Singh, 1981). Therefore study of specific PCB congeners based on their structure will be needed, because the most toxicologically active PCB congeners are those having chlorine substitution at the para (4 and 4') position and no ortho (2,2',6 and 6') positions on the biphenyl moiety. For instance, coplanar chlorobiphenyls (#77, 81, 126 and 169) might be highly toxic since they are most structurally simillar to 2,3,7,8-TCDD of all the congeners (Safe, 1987; Tenabe et al., 1987, 1989). The dioxin, 2,3,7,8-TCDD is generally considered the most potent synthetic environmental toxicant. Therefore reporting concentration data as total PCBs may not related well to the toxicity of PCBs and may be mislead.

As microwave oven is getting a popular kitchen appliance, and there are a lot of varieties of microwavable food in the market, the study of effectiveness in reduction

of harmful chemicals by microwave cooking is also necessary.Zabik et al. (1979) cooked lake trout (ciscowet) by microwave and reduced the PCBs by an average of 26%, even though they did not show a significant differences in reduction of PCBs, comparing to other cooking methods; broiling, roasting. Cooking by microwave using different cooking times and more comparison of effectiveness of PCB reduction with other cooking methods are needed to be researched.

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APPENDICES

Appendix 1. Systematic Numbering of PCB Compounds

No.	Structure	No.	Structure
	Monochlorobiphenyls		Tetrachlorobiphenyls
1	2	40	2,2',3,3'
2	3	41	2,2',3,4
3	4	42	2,2',3,4'
		43	2,2',3,5
	Dichlorobipheynls	44	2,2',3,5'
4	2,2	45	2,2',3,6
5	2,3	46	2,2',3,6'
6	2,3'	47	2,2',4,4'
7	2,4	48	2,2',4,5
8	2,4'	49	2,2',4,5'
9	2,5	50	2,2',4,6
10	2,6	51	2,2',4,6'
11	3,3'	52	2,2',5,5'
12	3,4	53	2,2',5,6'
13	3,4'	54	2,2',6,6'
14	3,5	55	2,3,3',4
15	4,4'	56	2,3,3',4'
		57	2,3,3',5
	Trichlorophenyls	58	2,3,3',5'
16	2,2',3	59	2,3,3',6
17	2,2',4	60	2,3,4,4'
18	2,2',5	61	2,3,4,5
19	2,2',6	62	2,3,4,6
20	2,3,3'	63	2,3,4',5
21	2,3,4	64	2,3,4',6
22	2,3,4'	65	2,3,5,6
23	2,3,5	66	2,3,4,4'
24	2,3,6	67	2,3,4,5
25	2,3',4	68	2,3,4,5'
26	2,3',5	69	2,3,4,6
27	2,3',6	70	2,3,4',5
28	2,4,4'	71	2,3,4',6
29	2,4,5	72	2,3,5,5'
30	2,4,6	73	2,3,5',6
31	2,4',5	74	2,4,4',5
32	2,4',6	75	2,4,4',6
33	2',3,4	76	2',3,4,5
34	2',3,5	77	3,3',4,4'
35	3,3',4	78	3,3',4,5
36	3,3',5	79	3,3',4,5'
37	3,4,4'	80	3,3',5,5'
38	3,4,5	81	3,4,4',5
39	3,4',5		

Appendix 1---continued

No.	Structure	No.	Structure
	Pentachlorobiphenyls		
82	2,2',3,3',4	121	2,3',4,5',6
83	2,2',3,3',5	122	2',3,3',4,5
84	2,2',3,3',6	123	2',3,4,4',5
85	2,2',3,4,4'	124	2',3,4,5,5'
86	2,2',3,4,5	125	2',3,4,5,6'
87	2,2',3,4,5'	126	3,3',4,4',5
88	2,2',3,4,6	127	3,3',4,5,5'
89	2,2',3,4,6		
90	2,2',3,4',5		Hexachlorobiphenyls
91	2,2',3,4',6	128	2,2',3,3',4,4'
92	2,2',3,5,5'	129	2,2',3,3',4,5
93	2,2',3,5,6	130	2,2',3,3',4,5'
94	2,2',3,5,6'	131	2,2',3,3',4,6
95	2,2',3,5',6	132	2,2',3,3',4,6'
96	2,2',3,6,6'	133	2,2',3,3',5,5'
97	2,2',3'4,5	134	2,2',3,3',5,6
98	2,2',3'4,6	135	2,2',3,3',5,6'
99	2,2',4,4',5	136	2,2',3,3',6,6'
100	2,2',4,4',6	137	2,2',3,4,4',5
101	2,2',4,5,5'	138	2,2',3,4,4',5'
102	2,2',4,5,6'	139	2,2',3,4,4',6
103	2,2',4,5',6	140	2,2',3,4,4',6'
104	2,2',4,6,6'	141	2,2',3,4,5,5'
105	2,3,3',4,4'	142	2,2',3,4,5,6
106	2,3,3',4,5	143	2,2',3,4,5,6'
107	2,3,3',4,5	144	2,2',3,4,5',6
108	2,3,3',4,5'	145	2,2',3,4,6,6'
109	2,3,3',4,6	146	2,2',3,4',5,5'
110	2,3,3',4'6	147	2,2',3,4',5,6
111	2,3,3',5,5'	148	2,2',3,4',5,6'
112	2,3,3,5',6	149	2,2',3,4',5',6
113	2,3,3',4',6	150	2,2',3,4',6,6'
114	2,3,4,4',5	151	2,2',3,5,5',6
115	2,3,4,5,6	152	2,2',3,5,6,6'
116	2,3,4,5,6	153	2,2',4,4',5,5'
117	2,3,4',5,6	154	2,2',4,4',5,6
118	2,3',4,4',5	155	2,2',4,4',6,6'
119	2,3',4,4',6	156	2,3,3',4,4',5
120	2,3',4,5,5'	157	2,3,3',4,4',5

Appendix 1.---continued

No.	Structure	No.	Structure
	Hexachlorobiphenyls		Octachlorobiphenyls
158	2,3,3',4,4',6	194	2,2',3,3',4,4',5,5'
159	2,3,3',4,5,5'	195	2,2',3,3',4,4',5,6
160	2,3,3',4,5,6	196	2,2',3,3',4,4',5',6
161	2,3,3',4,5',6	197	2,2',3,3',4,4',6,6'
162	2,3,3',4',5,5'	198	2,2',3,3',4,5,5',6
163	2,3,3',4',5,6	199	2,2',3,3',4,5,6,6'
164	2,3,3'4',5',6	200	2,2',3,3',4,5',6,6'
165	2,3,3',5,5',6	201	2,2',3,3',4',5,5',6
166	2,3,4,4',5,6	202	2,2',3,3',5,5',6,6'
167	2,3',4,4',5,5'	203	2,2',3,4,4',5,5',6
168	2,3',4,4',5',6	204	2,2',3,4,4',5,6,6'
169	3,3',4,4,5,5'	205	2,2',3',4,4',5,5',6
	Heptachlorobiphenyls		Nonachlorobiphenyls
170	2,2',3,3',4,4',5	206	2,2',3,3',4,4',5,5',6
171	2,2',3,3',4,4',6	207	2,2',3,3',4,4',5,6,6'
172	2,2',3,3',4,5,5'	208	2,2',3,3',4,5,5',6,6'
173	2,2',3,3',4,5,6		
174	2,2',3,3',4,5,6'		Decachlorobiphenyls
175	2,2',3,3',4,5',6	209	2,2',3,3',4,4',5,5',6,6'
176	2,2',3,3',4,6,6'		
177	2,2',3,3',4,5,6		
178	2,2',3,3',5,5',6		
179	2,2',3,3',5,6,6'		
180	2,2',3,4,4',5,5'		
181	2,2',3,4,4',5,6		
182	2,2',3,4,4',5,6'		
183	2,2',3,4,4',5',6		
184	2,2',3,4,4',6,6'		
185	2,2',3,4,5,5',6		
186	2,2',3,4,5,6,6'		
187	2,2',3,4,5,5',6		
188	2,2',3,4,5,6,6'		
189	2,3,3',4,4',5,5'		
190	2,3,3',4,4',5,6		
191	2,3,3',4,4',5',6		
192	2,3,3',4,5,5',6		
193	2,3,3',4,5,5',6		

Appendix 2. Protocol for Fish Processing in Meat Laboratory

All fish were received at the Michigan State University Meat Laboratory. The containers should be placed in a 0°C cooler. All fish should be processed within 24 hours of receipt. It was hoped that processing can occur as soon as possible after the fish have been received. Each fish were received head off with gills, kidney and viscera removed. Wherever practically possible, the fish flesh should not be exposed to plastic. The fish were identified as to right and left side.

All fish should go through the following process protocol:

1. If dirt or contamination existed on the surface, the fish was washed or rinsed in cold water.
2 Appropriate random sample fish were selected.
3. All fish contributing to skin-on fillets were scaled and washed.
4. Belly flaps were removed up to the ribs.
5. All fish were filleted with rib bones removed last. In skin-on fillets, the fatty back strip from the appropriate area of fillet was removed carefully.
6. In skin-off fillets, the skin was removed and all dark tissue was trimmed away including the dark tissue from the lateral line. The fish pieces were appropriately

labeled with the random numbers.

7. Left sides for cooking portion were wrapped in aluminum foil and vacuum packaged. Labels were placed both in the interior and on the outside of the package. The packages were frozen at -34°C.
8. Right sides for raw samples (skin-on or skin-off) were ground to a uniform particle size. The method of particle reduction was grinding, chopping, or blending appropriately at a frozen state.
9. All raw ground fish were placed in glass containers, covered with aluminum foil, and appropriately capped.
10. The random number was labeled on the inside of the cap and was placed on a tape label on the outside of the container.
11. All samples were stored immediately at -34°C and held for transport to appropriate laboratories.

Appendix 3. Size, Processing and Cooking data for Carp from Lake Erie and Huron. Fish Cooked both with Skin-on and Skin-off.

	Cooking Methods			
	Skin-on		Skin-off	
	Pan Fry	Deep Fat Fry	Pan fry	Deep Fat Fry
	Lake Erie			
Weight (g)	1813±337[1]	1813±337	1855±404	1855±404
Length (cm)	52.3±4.5	52.3±4.5	51.2±3.6	51.2±3.6
Carcass Yield %	57.5±3.5	57.5±3.5	--- ---	--- ---
As Prepared Yield %	36.3±3.4	36.3±3.4	25.6±2.7	25.6±2.7
Total Cooking Loss %	22.6±4.8	32.9±5.9	21.6±5.3	36.5±4.9
Cooking Yield %	68.5±3.1[2]	67.1±5.9	78.4±5.3	63.5±4.9
	Lake Huron			
Weight (g)	1567±398	1653±442	1482±587	1625±521
Length (cm)	46.7±4.0	48.0±4.6	45.5±5.4	46.1±4.9
Carcass Yield %	58.4±1.9	58.0±2.0	62.2±1.4	61.3±2.1
As Prepared Yield %	29.0±2.9	29.1±2.8	22.0±1.6	21.5±1.7
Total Cooking Loss %	20.1±5.0	30.2±5.4	15.1±3.1	30.4±3.8
Cooking Yield %	68.9±5.0	69.8±5.4	84.9±3.1	69.6±3.8

[1]Mean and standard deviation, n=6
[2]Skin included with fillet for deep fat fried fish only.

Appendix 4. HPLC Pump Operating Conditions

-HPLC Pump-

1. Turn on Waters/590 Programmable HPLC Pump.
2. Set to manual mode by (page 3.2.2 of manual).
   A. Push blue "2nd func" button
   B. Push manual (next Param) button
3. Set flow to 4.000 mL/min (page 3.2.2 of manual)
   A. Push "next Param" button until readout indicates "flow X.XXX mL"
   B. Push "4" button
   C. Push "Enter" button
4. Make sure methylen chloride, brown solvent reservoir is full. If not:
   A. Filter HPLC grade methylen chloride through HPLC filter flask.
   B. Fill solvent reservoir.
5. Make sure the air bubbles in plastic inlet line between methylen chloride reservoir and HPLC pump are out. If air in the line: (page 2-10 of the manual)
   A. Attach high pressure, 10 mL syringe to plastic tube at the draw off valve on pump with plunger in.
   B. Turn black plastic knob counterclockwise 3-4 turns.
   C. Pull out on syringe and empty.
6. Set pressure limits (page 3-4 of manual).

A. Set low limit to 0.

B. Set high limit to 600.

7. set compressibility compensation (page 2-5 of manual). Set to 0.

8. In case of problems (pressure overload, etc.) see manual.

-Automatic Injector-

1. Turn on Waters 712 Wisp (bottom red button).

2. Set to auto mode (red LED on at auto).

3. Set sample number to 0 (page 4-5 of manual).

A. Press down "sample No." key and release.

B. Press down "0" key and release.

C. Press down "Enter" key and release.

4. Set system message for auxiliary loop (page 4-7 of manual).

A. Press "Sys Mes" key and release.

B. Using numeric key enter 71.

C. Press "Enter" key and release.

D. Using numeric key enter 01.

E. Press "Enter" key and release.

F. system message display should read 7101.

5. Set injection volume (page 4-6 of manual).

A. Press down "Inj vol" key and release.

B. Using numeral keys enter 200 uL.

C. Press down "Enter" key and release.

6. Set run time (page 4-8 of manual).

A. Press "Run Time" key and release.

B. Using numeric keys enter 25 minutes.

C. Press "Enter" key and release.

7. Set Equilibration Delay (page 4-9 of manual).

A. Press "Sys Mes" key and release.

B. Using numeric keys enter 0000.

C. Press "Enter" key and release.

8. Set number of injections (page 4-10 of manual).

A. Press "No of Inj" key and release.

B. Using numeric key enter 1.

C. Press "Enter" key and release.

9. Set syringe speed (page 4-14 of manual).

A. Press "Sys Mes" key and release.

B. Using numeric keys enter 76.

C. Press "Enter" key and release.

D. Using numeric key enter 1 for event maker speed.

E. Press "Enter" key and release.

10. Set mark width (page 4-10 of manual).

A. Press "Sys Mes" key and release.

B. Using numeric keys enter 78.

C. Press "Enter" key and release.

D. Using numeric key enter 04.

E. Press "Enter" key and release.

F. System message display should read 7804.

-Fraction Collector-

1. Turn on Waters fraction collector (press green "Power" key.
2. Press red "End" key.
3. Press red/black "C/M" key.

Approved by Dr. Matthew Zabik

Appendix 5. PCB Standard Congener preparation for Gas Chromatography

Congener #	Structure	Congener #	Structure
30	2,4,6	114	2,3,4,4',5
31	2,4',5	118	2,3',4,4',5
42	2,2',3,4	120	2,3',4,5,5'
44	2,2',3,5'	121	2,3',4,5',6
47	2,2',4,4'	122	2',3,3',4,5
49	2,2',4,5'	128	2,2',3,3',4,4'
52	2,2',5,5'	132	2,2',3,3',4,6'
55	2,3,3',4	136	2,2',3,3',6,6'
66	2,3',4,4'	137	2,2',3,4,4',5
70	2,3',4',5	138	2,2',3,4,4',5
72	2,3',5,5'	141	2,2',3,4,5,5'
76	2',3,4,5	149	2,2',3,4',5',6
79	3,3',4,5'	153	2,2',4,4',5,5'
83	2,2',3,3',5	157	2,3,3',4,4',5'
84	2,2',3,3'6	158	2,3,3',4,4',6
85	2,2',3,4,4'	167	2,3',4,4',5,5'
87	2,2',3,4,5	171	2,2',3,3',4,4',6
91	2,2',3,4',6	179	2,2',3,3',5,6,6'
92	2,2',3,5,5'	180	2,2',3,4,4',5,5'
95	2,2',3,5',6	181	2,2',3,4,4',5,6
97	2,2',3',4,5	183	2,2',3,4,4',5',6
99	2,2',4,4',5	185	2,2',3,4,5,5',6
101	2,2',4,5,5'	190	2,3,3',4,4',5,6
103	2,2',4,5',6	198	2,2',3,3',4,5,5',6
105	2,3,3',4,4'	200	2,2',3,3',4,5',6,6'
108	2,3,3',4,5'		
110	2,3,3',4',6		

Appendix 6-1. Analysis of General Linear Models - Carp Length Analysis

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Cook Method	2	Pan fry	Deep fat fry
Skin	2	Skin-on	Skin-off

Source	DF	Mean Square	F value	Pr > F
lake	1	321.37	13.70	0.0006
cook method	1	2.71	0.12	0.7359
lake*cook method	1	2.71	0.12	0.7359
skin	1	20.02	0.85	0.3612
lake*skin	1	0.61	0.03	0.8730
cook method*skin	1	0.30	0.01	0.9104
lake*cook method*skin	1	0.30	0.01	0.9104

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	51.750	24	Erie
B	46.575	24	Huron

Appendix 6-2. Analysis of General Linear Models - Carp Carcass Yield Analysis

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Cook Method	2	Pan fry	Deep fat fry
Skin	2	Skin-on	Skin-off

Source	DF	Mean Square	F value	Pr > F
lake	1	49.04	6.44	0.0166
cook method	1	1.64	0.22	0.6462
lake*cook method	1	0.82	0.11	0.7453
skin	1	77.54	10.18	0.0033
lake*skin	0	.	.	.
cook method*skin	1	0.42	0.06	0.8146
lake*cook method*skin	0	.	.	.

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	61.787	24	Skin-on
B	57.853	12	Skin-off

Appendix 6-3. Analysis of General Linear Models - Carp As Prepared Yield Analysis

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Cook Method	2	Pan fry	Deep fat fry
Skin	2	Skin-on	Skin-off

Source	DF	Mean Square	F value	Pr > F
lake	1	157.65	16.37	0.0002
cook method	1	40.09	4.16	0.0479
lake*cook method	1	40.09	4.06	0.0479
skin	1	599.75	62.29	0.0001
lake*skin	1	152.40	15.83	0.0003
cook method*skin	1	36.87	3.83	0.0574
lake*cook method*skin	1	36.87	3.83	0.0574

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	32.663	24	Skin-on
B	25.593	24	Skin-off

Appendix 6-4. Analysis of General Linear Models - Carp Cook Loss Analysis

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Cook Method	2	Pan fry	Deep fat fry
Skin	2	Skin-on	Skin-off

Source	DF	Mean Square	F value	Pr > F
lake	1	238.74	8.45	0.0059
cook method	1	1912.56	67.72	0.0001
lake*cook method	1	0.01	0.00	0.9838
skin	1	3.68	0.13	0.7200
lake*skin	1	40.06	1.42	0.2407
cook method*skin	1	70.35	2.49	0.1224
lake*cook method*skin	1	0.31	0.01	0.9177

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	28.404	24	Erie
B	23.944	24	Huron
A	32.486	24	Deep fat fry
B	19.862	24	Pan fry

Appendix 6-5. Analysis of General Linear Models - Carp Cook Yield Analysis.

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry

Source	DF	Mean Square	F value	Pr > F
cook method	1	703.11	26.84	0.0001
lake*cook method	1	2.95	0.11	0.7392
skin	1	366.14	13.97	0.0006
lake*skin	1	66.48	2.54	0.1190
cook mrthod*skin	1	655.57	25.02	0.0001
lake*cook method*skin	1	5.65	0.22	0.6449

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	75.168	24	Pan fry
B	67.514	24	Deep fat fry

Appendix 6-6. Analysis of General Linear Models - Total PCB Congeners Analysis (ppm wet).

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry
Product	2	Raw	Cooked

Source	DF	Mean Square	F value	Pr > F
lake	1	8.67	6.49	0.0126
skin	1	10.26	7.68	0.0068
cook method	1	5.37	4.02	0.0479
product	1	0.74	0.56	0.4582
lake*skin	1	6.04	4.52	0.0363
lake*cook method	1	12.51	9.37	0.0029

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	1.659	48	Raw
A	1.483	48	Cooked
A	1.872	48	Erie
B	1.271	48	Huron

Appendix 6-6 --- continued

Tukey Grouping	Mean	N	
A	1.898	48	Skin-on
B	1.244	48	Skin-off
A	1.808	48	Deep fat fry
B	1.335	48	Pan fry

Appendix 6-7. Analysis of General Linear Models - Total PCB Congeners Analysis (ppm dry).

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry
Product	2	Raw	Cooked

Source	DF	Mean Square	F value	Pr > F
lake	1	121.43	9.87	0.0023
skin	1	72.55	5.90	0.0172
cook method	1	28.27	2.30	0.1330
product	1	167.61	13.63	0.0004
lake*skin	1	31.87	2.59	0.1110
lake*cook method	1	99.97	8.13	0.0054

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	6.546	48	Raw
B	3.904	48	Cooked
A	6.350	48	Erie
B	4.100	48	Huron

Appendix 6-7 --- continued

Tukey Grouping	Mean	N	
A	6.094	48	Skin-on
B	4.356	48	Skin-off
A	5.768	48	Pan fry
A	4.682	48	Deep fat fry

Appendix 6-8. Analysis of General Linear Models - Total PCB Congeners Analysis (ug wet).

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry
Product	2	Raw	Cooked

Source	DF	Mean Square	F value	Pr > F
lake	1	267456.32	7.22	0.0086
skin	1	371641.55	10.04	0.0021
cook method	1	68485.40	1.85	0.1773
product	1	171581.88	4.63	0.0341
lake*skin	1	194190.90	5.24	0.0244
lake*cook method	1	244653.74	6.61	0.0118

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	230.00	48	Raw
B	145.44	48	Cooked
A	240.50	48	Erie
B	134.94	48	Huron

Appendix 6-8 --- continued

Tukey Grouping	Mean	N	
A	249.94	48	Skin-on
B	125.50	48	Skin-off
A	214.43	48	Deep fat fry
A	161.01	48	Pan fry

Appendix 6-9. Analysis of General Linear Models - Total PCB Congeners Analysis (% Change).

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry

Source	DF	Mean Square	F value	Pr > F
lake	1	8.98	0.05	0.8311
skin	1	116.50	0.60	0.4438
cook method	1	755.09	3.88	0.0559
lake*cook method	1	5.11	0.03	0.8722
lake*skin	1	626.84	3.22	0.0804
skin*cook method	1	139.26	0.71	0.4028
lake*skin*cook method	1	1461.25	7.50	0.0092

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	35.734	48	Skin-on
A	32.618	48	Skin-off
A	38.142	48	Deep fat fry
A	30.210	48	Pan fry

Appendix 6-10. Analysis of General Linear Models - Total PCB Congeners Analysis (ug wet).

Class Level Information

Class	Level		
Lake	2	Erie	Huron
Skin	2	Skin-on	Skin-off
Cook Method	2	Pan fry	Deep fat fry
Product	2	Cooked	Raw

Source	DF	Mean Square	F value	Pr > F
lake	1	267456.32	7.22	0.0086
skin	1	371641.55	10.04	0.0021
cook method	1	68485.40	1.85	0.1773
product	1	171581.88	4.63	0.0341
lake*skin	1	194190.90	5.24	0.0244
lake*cook method	1	244653.74	6.61	0.0118

< Tukey's Studentized Range Test >

Tukey Grouping	Mean	N	
A	230.00	48	Raw
B	145.44	48	Cooked
A	249.94	48	Skin-on
B	125.50	48	Skin-off

Appendix 6-10 --- continued

Tukey Grouping	Mean	N	
A	214.43	48	Deep fat fry
A	161.01	48	Pan fry