Bull. Environm. Contam. Toxicol. 28, 592–598 (1982)

Predictability of PCBs in Carp Harvested in Saginaw Bay, Lake Huron*

Mary E. Zabik, Cynthia Merrill, and Matthew J. Zabik

Department of Food Science and Human Nutrition and Pesticide Research Center, Michigan State University, East Lansing, MI 48824

Recent data from the GREAT LAKES ENVIRONMENTAL CONTAMINANTS SURVEY (1979) indicated that PCBs varied from 0.2 to 8.0 ppm in edible fillets of carp (Cyprinus carpio) harvested in Lake Huron while dieldrin and DDT levels were low ranging from 0.00 to 0.04 and 0.0 to 2.1 ppm, respectively. The Environmental Protection Agency published its intention to reduce the levels of PCBs from 5 to 2 ppm in edible fish fillets in 1977. This order took effect in spring of 1979 but was rescinded for fish later that fall.

Since carp are caught commercially in Saginaw Bay, the purpose of this research was to quantitate the level of xenobiotics in carp and particularly to determine if the level of PCBs in the fish could be predicted to aid fisherman in determining the size of fish which could be caught with levels of PCBs which would likely be below tolerance.

EXPERIMENTAL

Commercially caught carp were purchased during 1979 and 1980 and transported within 24 hrs of harvesting under ice to Michigan State University. Fish were weighed and measured before cleaning. The entire fillet from the right side of each fish was minced in Hobart Food Chopper, model 84181D, before a representative sample of a the homogeneous ground flesh was frozen in glass at -23°C for later xenobiotic analyses. A total of 211 fish representing all seasons of the year were divided into 4 size ranges < 2.0 kg (n=40); 2.01 to 4.0 kg (n=78); 4.01 to 5.5 kg (n=62) and > 5.5 kg (n=31). This corresponds approximately to the following: < 4.5 lb, 4.5 - 9 lb, 9 - 12 lb, and > 12 lb, respectively.

Samples were thawed at 4-5°C for 24 hours before hexane-acetone extraction, acetonitrile partitioning and florisil-celite column cleanup according to the procedures outlined by YADRICK et al. (1972). An aliquot of the hexane was dried under vaccuum at 70°C to estimate fat. Following final

Michigan Agricultural Experiment Station Journal Article No. 10269.

0007-4861/82/0028-0592 $01.40

concentration, PCBs, dieldrin, and DDT were quantitated using a Tracor 560 gas chromatograph (GLC) equipped with a ^{63}Ni electron capture detector. The column for the GLC was a Pyrex column, 1.83 m long X 4.0 mm wide, packed with 4% SE 30 plus 6% OV 210 on 80/100 mesh Chrom Sorb W-HP. The carrier gas was nitrogen with the flow rate of 40 ml/min. Temperatures at the injection port, column and detector were 230, 190 and 300°C, respectively. Standards were prepared with 99 + % pure recrystallized dieldrin, p,p' DDT and p,p' DDE in nanograde hexane. Preliminary GLC analyses revealed that a 1:1 mixture of Aroclor 1248 and 1254 best matched the pattern of these PCB peaks thus this mixture was used throughout. Quantitations were based on the peak areas for pesticides correcting for overlap with PCBs, while the area for all PCB peaks from 3.0 to 10.0 min except those with retention times close to that of dieldrin and DDT Compounds was used to quantitate PCBs. Standards were run at the beginning of the day and after every 6 to 8 samples. Recoveries of PCB from ocean perch spiked with 0.5 to 5 ppm of this mixture averaged 83%. Presence of these residues was confirmed by mass spectrometric analyses. Mass spectrometric analysis was done on a pool of fish extractions from each size group. A Beckman GC-65 gas chromatograph interfaced with a DuPont 21-490 mass spectrometer was used. The mass spectra was obtained at an ionizing voltage of 70 eV with a source temperature of 210°C.

PCBs and pesticides were expressed on an edible tissue and fat basis. To predict the level of PCBs in the fish, LS and LSSTEP program was run on MSU's Cyber 750 Computer. The LS program allowed the computer to choose the most significant single correlation and then from partial correlations using the first factor, additional items were added to improve the predictability of the equation. Items in the pool included each of the physical parameters, percentage fat, quadratic expressions of these items and interactive terms of these items. The LS step program forced the computer to start with one designated item, i.e. weight, afterwhich the computer was free to add any item which would improve the predictability.

RESULTS AND DISCUSSION

Levels of Xenobiotics in Carp

The size and sex of the various carp caught during the four seasons are given in Table 1. Of the fish analyzed only 31% were male. Size was fairly consistant among the four seasons except for the largest size group in which the largest fish were caught in the fall. It was most difficult to obtain fish in the winter with only 14% of the sample obtained during that season. Carp were most abundant in fall (43%) and equally available during the spring (22%) and summer (21%).

As expected fat content increased as the size of the carp increased (Table 2); however wide ranges in fat content occurred

Table 1. Size and sex of carp analyzed for xenobiotics.

Size Group	Season	Weight Mean ± s.d. kg	Length mean ± s.d. cm.	Sex: Male (Nos.)	Sex: Female (Nos.)
< 2 kg	All	1.4±.4	46.0±4.9	26	14
	Spring	1.6±.4	49.1±4.5	9	3
	Summer	1.4±.4	45.4±4.8	7	6
	Fall	1.3±.4	43.6±4.1	9	4
	Winter	1.8±.6	49.3±3.2	1	1
2-4 kg	All	3.2±.5	60.0±4.6	26	52
	Spring	3.1±.6	58.0±4.8	4	11
	Summer	2.9±.5	59.7±3.9	5	8
	Fall	3.3±.5	59.8±4.8	6	27
	Winter	3.3±.5	60.1±4.8	11	6
4-5.5 kg	All	4.6±.7	67.0±3.3	11	51
	Spring	4.9±.5	68.3±3.1	4	12
	Summer	4.5±.5	66.0±3.6	3	14
	Fall	4.7±.5	66.9±3.3	3	20
	Winter	4.6±.3	66.4±1.8	1	7
> 5.5 kg	All	7.2±2.5	75.7±5.9	3	28
	Spring	6.4±.3	74.0±1.9	1	4
	Summer	6.0±.2	75.2±2.8	1	2
	Fall	7.6±2.9	76.3±6.9	1	20
	Winter	6.6±.5	75.2±4.5	-	2

Table 2. Fat, PCBs, and DDT compounds in edible tissue of carp.

Size Group	Fat %	Xenobiotic Levels: PCBs ppm	DDE ppm	DDT ppm
< 2 kg	2.89±2.00	.262±.253	.016±.018[a]	.003±.012[b]
2 - 4 kg	6.77±3.39	.896±.733	.053±.066[c]	.004±.014[d]
4 - 5.5 kg	7.54±3.94	.899±.764	.043±.060[e]	.011±.034[f]
> 5.5 kg	9.04±4.75	.834±.890	.080±.068[g]	.003±.009[h]

[a] Nondetectable in 1 fish
[b] Nondetectable in 27 fish
[c] Nondetectable in 5 fish
[d] Nondetectable in 47 fish
[e] Nondetectable in 9 fish
[f] Nondetectable in 31 fish
[g] Nondetectable in 2 fish
[h] Nondetectable in 27 fish

in each size range. DDE occurred in most fish at low levels whereas DDT levels were often nondetectable. Only 31% of the fish under 2 Kg, 39% of fish from 2.01 to 4 Kg, 51% of the fish from 4.01 to 5.5 Kg and 13% of the fish $>$ 5.5 Kg had measureable quantities of DDT. Dieldrin was found in less than one percent of the fish. PCB levels also tended to be low although again wide variations occurred with the lowest value being 0.01 ppm and the highest 4.79 ppm. Only in the carp below 2 Kg wt. did none of the fish exceed 2 ppm. Moreover means and standard deviations of each of the three larger groups of carp were suprisingly similar.

Predictability of the PCB Levels in Carp

When the PCB levels of the entire sample were related to weight, length, percentage fat, sex, season, as well as the interactions of each of these terms and quadratic relationships, only 32% of the variation in the data could be explained by the resulting prediction equation. Therefore it was decided to see if the variation within each size group was predictable.

For the carp under 2 kg in size the regression analyses were highly significant ($p < .0005$) with 90% of the variation predicted by all of the factors. A simplified equation predicting 73% of the variability is:

$$\text{ppm PCBs} = -1.328\frac{WF}{(W+F)} + 0.018\,LF - 0.236\,SxF + 0.353\,SxW - 0.030\,F^2 - 0.008\,LW + 0.2323$$

where W = weight
F = percentage fat
L = length
Sx = sex of fish.

The regression analyses for the carp from 2.0 to 4.0 kg was not significant and only 29% of the variation in this size group could be predicted. Nevertheless, the regression analysis for the carp from 4.0 to 5.5 kg was highly significant ($p < 0.0005$) but slightly less predictable (68%) from all the components in the analyses. None of the simplified LS Step equations predicted more than 32% of the variation so the complete equation is given:

$$\text{ppm PCB} = 0.334L - 648.207\,W - 10.235F - 11.790\,Sx + 0.353\,Sn + 0.018L^2 + 9.165\,W^2 + 0.173\,F^2 - 1.276\,LW - 0.161\,LF - 1.128\,WF - 0.281\,SxW + 0.183\,SxF + .003SnL - 0.160\,SnW + 0.014\,SnF + 0.136\,SnSx + 0.178\,SxL + 0.022\,LWF + 742.718\frac{LW}{L+W} + 21.531\frac{WF}{W+F} - 4.260\frac{WF}{W+F} - 114.035.$$

where L = length
W = weight
F = percentage fat
Sx = sex of fish
Sn = season of year

Finally the regression analyses for the carp > 5.5 kg were significant (p =<.05) and the prediction equation with all factors accounted for 85% of the variability. A simplified equation accounting for 75% of the variability is:

$$\text{ppm PCB} = 1.292\,L + .002\,LWF - 0.197\,WF - 0.009L^2 + .008F^2 - 42.916$$

where L = length
W = weight
F = percentage fat.

Season of catch and sex may also affect the predictability of PCBs since their means and standard deviation varied (Table 3). When fish of all sizes were separated by season of catch,

Table 3. Means and standard deviations of carp listed by season of catch and sex of fish.

Variable	Number	PCBs ppm
Season:		
Spring	48	.706 ± .667
Summer	46	.651 ± .609
Fall	90	.781 ± .867
Winter	27	1.031 ± .717
Sex:		
Male	66	0.712 ± .706
Female	145	0.793 ± .781

59% of the variability for spring, 67% for summer, 35% for fall, and 68% for winter could be predicted. Thus, better predictability had been obtained from size divisions. Even though most of the male fish were in the small size group, the mean PCB level for this group was only 0.1 ppm below that of the females. Total predictability of carp from all sizes separated by sex was 52% for the males but only 29% for the females. Thus size of carp, again, is the best division to use to separate factors capable of predicting PCBs.

Finally since a fisherman would not know the percentage of fat which has been an important factor in each prediction equation, simple correlations of PCBs to length or weight factors were reviewed. For all fish the correlation coefficient with length was 0.277 and with weight was 0.255. Only components with fat had higher correlation coefficients. As can be seen from Table 4, correlation was best for length for carp < 2 kg, weight for carp between 4-5.5 kg and length for carp > 5.5 kg. Moreover ppm of PCBs in carp correlated better with weight and length in spring and summer. In addition, PCBs correlated much better to size parameters in males than in females. There

Table 4. Correlation coefficients of ppm PCBs with length and weight of carp.

Grouping		Correlation Coefficient Length	Weight
Size:	< 2 kg	0.480	0.371
	2-4 kg	-0.096	0.110
	4-5.5 kg	0.167	-0.425
	> 5.5 kg	0.420	0.192
Season:	Winter	-0.141	-0.133
	Spring	0.474	0.471
	Summer	0.483	0.451
	Fall	0.190	0.193
Sex:	Male	0.512	0.532
	Females	0.178	0.183

may be an interrelationship among size of fish, time of year caught and sex of fish. This may have contributed greater predictability for the fish < 2 kg in size, since close to a majority of the fish which were male were caught in the spring or summer. Other sizes were completely scattered.

Thus of the 211 carp obtained commercially from Saginaw Bay, none exceeded the current tolerance of 5 ppm PCBs in edible fillet. However, had not the reduction to 2 ppm not been rescinded, some carp in all size groups except the smallest exceeded 2 ppm. Prediction equations were calculated which accounted for a 68 to 90 percent of PCB variability in many groups. The carp from 2 to 4 Kg were less predictable as to their level of PCBs as were carp caught in the fall or females. The percentage fat was an important component of these prediction equations. Length of fish correlated better with PCB for carp <2 kg and > 5.5 kg while weight correlated better for fish 4 to 5.5 kg. Correlations were highest for spring and summer catchs and for males. Thus size alone could be a reasonably good predictor of PCBs caught during the spring and summer but is less so the rest of the year.

ACKNOWLEDGEMENT

This publication is a result of work sponsored by the Michigan Sea Grant Program, project number R/GLF-2, with a grant, NA-80-AA-D-00072, from the Office of Sea Grant National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, and funds from the State of Michigan. The U.S. Government is authorized to produce and distribute reprints for governmental purposes not withstanding any copyright notation appearing hereon.

REFERENCES

GREAT LAKES ENVIRONMENTAL CONTAMINANTS SURVEY: 1976-1977 Michigan Department of Agriculture, Lansing, Michigan (1979).

YADRICK, M.K. K. FUNK and M.E. ZABIK: J. Agric. Food Chem. 19, 491 (1971).