Bull. Environm. Contam. Toxicol. 30, 65–73 (1983)

PCB, DDT, and Benzo(a)pyrene in Raw and Pan-fried White Croaker (*Genyonemus lineatus*)

Harold W. Puffer[1] and Richard W. Gossett[2]

[1]Department of Pathology, School of Medicine, University of Southern California, Los Angeles, CA 90033, and [2]Trace Organics Laboratory, Southern California Coastal Water Research Project, Long Beach, CA 90806

A major survey of southern California sportfishermen was conducted in 1978 by the California Department of Fish and Game (WINE 1979). Wine found that over one-million angler trip hours per year were expended on fishing and one in three fish caught was white croaker (Genyonemus lineatus). A major portion of those fish was caught in waters of Santa Monica Bay where there has been considerable concern regarding the water quality and pollution.

Santa Monica Bay's water quality is influenced by many factors including two large wastewater outfalls (Hyperion and the Joint Water Pollution Control Plant [JWPCP]), a sludge outfall, discharge from power plants, an oil refinery, a harbor, surface run-off by rain and storms, aerial fallout, public use of beaches, and small boat activity (BASCOM 1980). Prior to 1971 the rate of DDT discharged out the JWPCP outfall was estimated to be 21.6 metric tons per year. Since 1971 the rate has been reduced to about 0.7 metric tons and has remained relatively constant (SMOKLER et al. 1979; EIS/EIR 1980). Although the discharge of DDT has been reduced, the sediments adjacent to the outfall still contain large deposits of this and other contaminants such as PCB and benzo(a)pyrene (BaP) and remain the major source of these contaminants to bottom feeding animals (GOSSETT et al. 1982a). In 1978 concentrations of total DDT and total PCB were measured at 1 mg/dry kg and 2 mg/dry kg, respectively, in Santa Monica Bay sediments from the site where the white croaker for this study were collected (YOUNG et al. 1980).

White croaker caught near the Joint Water Pollution Control Plant outfall in waters off Palos Verdes peninsula adjacent to Santa Monica Bay during April 1975 were clearly contaminated and contained mean concentrations of 39 ppm DDT and 2.8 ppm PCB in their edible muscle tissue (YOUNG, unpublished data). By 1980 these concentrations had dropped to 7.6 ppm and 0.38 ppm, respectively (GOSSETT et al. 1982b). Nevertheless, these concentrations remained of concern, particularly since

0007-4861/83/0030-0065 $01.80

a survey in 1980-81 by PUFFER et al. (1982) had confirmed the previous findings of WINE (1979) and had further shown that fishermen were consuming a large portion of the fish they were catching. They reported that the overall median consumption rate of fish being caught was 37 g/day/person annually and 10% were consuming 85 g/day/person for the entire year. The median consumption rate for fishermen surveyed at Santa Monica Bay was much higher, 97 g/day/person.

Using data for fish consumption reported by PUFFER et al. (1982) and the most recent data regarding DDT and PCB concentrations in white croaker, GOSSETT et al. (1982b), it was estimated that sportfishermen would consume 2.2 mg of total DDT and 1.9 mg of total PCB annually. This estimate was based on the consumption of uncooked fish. However, recent reports of the effect of cooking on PCB and DDT indicate that concentrations of these contaminants in carp and trout may be significantly altered by cooking (REINERT et al. 1972; ZABIK 1982). Several reports indicate that cooking of foods, including fish, significantly effects the content of substances such as carcinogens and mutagens (FABIAN 1968; KRONE & IWAOKA 1981; LIJINSKY & SHUBIK 1964, 1965; PARIZA et al. 1979; YAMAIZUMI et al. 1980). However, no studies have been made on the effect of cooking on concentrations of DDT and PCB in white croaker. PUFFER et al. (1982) found that pan frying was the major method of cooking used by sportfishermen consuming white croaker in the Los Angeles area. Therefore, it was decided to study the effect of pan frying on concentrations of PCB and DDT in edible portions of white croaker. BaP, another widespread environmental pollutant (NATIONAL ACADEMY OF SCIENCES 1972), was also included for analysis because several investigators have reported the presence of this compound in fried and broiled foods (LIJINSKY & SHUBIK 1964, 1965; NAGAO et al. 1977; FRITZ 1973). This paper describes the results of this study.

METHODS

Materials. White croaker (Genyonemus lineatus) was obtained by hook-and-line from waters of Santa Monica Bay and from Orange County. Samples from Santa Monica Bay were collected, May, 1981, 7 miles offshore of the Marine Del Rey breakwater near the end of the Hyperion Treatment Plant 7-mile outfall at 300 ft depth. The Orange County samples were collected, June 1981, at 200 ft depth approximately 1 mile south of Abalone Point. Fishing methods and sites were those used by local fishermen to assure that samples were representative of those obtained by sportfishermen.

Fish were skinned, filleted and fillets were weighed (9-38g) and measured (10-13cm length). Fillets from one side of fish were fried, composited and analyzed for DDT, PCB and BaP. Fillets from the opposite side of fish served as uncooked controls and were composited and analyzed using the same method as used for cooked tissues. Five composites of a total of 22 fillets from Orange County and 38 fillets from Santa Monica Bay were tested.

Cooking Procedure. White croaker fillets were pan fried in an electric skillet (West Bend 12 inch, 1255 watts, with non-stick coating) with 30 ml hydrogenated soybean oil (Wesson oil). Each fillet was fried for 4 min per side (8 min total cooking time) at a temperature of 190°C as described by KRONE & IWAOKA (1981). Temperature of the fillets during frying was measured using an iron constantin thermocouple.

DDT, PCB and BaP analysis. Percent dry weight was determined by freeze drying in a Lab Con Freeze-Dryer. Percent lipid was determined by chloroform/methanol extraction (BLIGH & DYER 1959). Samples analyzed for total DDT (ortho plus para isomers of DDT, DDE and DDD) and total PCB (Aroclor 1242 + Aroclor 1254) were homogenized with acetonitrile, filtered and re-extracted into hexane. Samples were further purified using a 6% ether in hexane elution on Florisil (MCB 60/100 mesh activated for four hours at 700°C).

PCB and DDT concentrations were determined using a Tracor MT220 gas chromatograph (GC) equipped with nickel 63 detectors with a makeup flow of 60 ml/min N_2. Chromatographic separation was performed on a 1.83 m x 2 mm ID glass column packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Gas-Chrom Q. The column was held at 200°C with a carrier flow rate of 20 ml/min N_2. Quantification was based on external standard peak height comparison with sample peak heights with the necessary correction for recovery. This laboratory confirms DDT and PCB results on a regular basis using gas chromatography mass spectrometry and all DDT results are corrected for PCB interference (LIU-HU et al. 1980). Our DDT and PCB results are not corrected for the interference of toxaphene. We have not detected toxaphene. In any case we had no indication it was present in concentrations high enough to affect our DDT or PCB results.

BaP was determined similar to the method reported by DUNN (1976) by homogenizing 25-50 g of tissue with ethanolic KOH and spiked with 25,000 counts of H^3BaP tracer. The homogenate was heated and then extracted with hexane. The extract was then added to a silica

column deactivated with 2% H_2O and eluted with toluene. Toluene was then removed by roto-evaporator and methanol was added and the extract sonicated. Finally 25% of the sonicated extract was analyzed by high pressure liquid chromatography using an Altex 420 reverse phase column with a 9:1 methanol/H_2O mobile phase and a 254 nm fixed wavelength detector. Quantification was based on an external standard and the remaining sample was archived. The limit of BaP detection was 1 ng.

RESULTS

Results of DDT and PCB analysis are presented in Table 1. Mean total DDT concentration ± standard error (SE) in uncooked fish samples from Santa Monica Bay was 0.60 ± 0.21 mg/wet kg and PCB concentration was 0.20 ± 0.04 mg/wet kg. Mean total DDT concentration ± SE after pan frying was 0.15 ± 0.04 mg/wet kg and mean PCB concentration ± SE was 0.070 ± 0.016 mg/wet kg. Mean total DDT concentration ± SE in uncooked fish samples from Orange County was 0.14 ± 0.04 mg/wet kg and PCB concentration ± SE was 0.018 ± 0.003 mg/wet kg. Mean total DDT concentration ± SE after pan frying was 0.085 ± 0.022 mg/wet kg and PCB concentration ± SE was 0.013 ± 0.002 mg/wet kg. The mean loss during cooking for fish samples from Santa Monica Bay was 74% DDT and 65% PCB and samples from Orange County was 39% DDT and 28% PCB. BaP was below detectable limits of 1 ug/wet kg in all cases.

Table 2 presents the percent dry weight and lipid/wet weight determinations before and after cooking of fish. The mean percent dry weight of uncooked fish samples from Santa Monica Bay was 24 and percent lipid/wet weight was 1.2. Mean percent dry weight after pan frying was 79 and percent lipid/wet was 19. The mean dry weight in the Orange County sample, also increased from uncooked to cooked samples, 21% to 73% respectively, and the mean lipid/wet weight increased from 0.89% to 19%.

DISCUSSION

It is apparent that pan frying has a prounced effect on DDT and PCB concentrations in white croaker fillets (Table 1). Total DDT in samples from Orange County was reduced 39% and total PCB was reduced 28%. Reduction in concentrations was even greater in samples from Santa Monica Bay; total DDT was reduced 74% and total PCB was reduced 65%. The greater relative loss in samples from Santa Monica Bay is most likely a function of concentration prior to pan frying. Initial concentrations of total DDT in white croaker taken at

Table 1. DDT and polychlorinated biphenyls (PCB) concentrations in uncooked and pan fried white croaker fillets (Genyonemus lineatus)

Composite No. (no. of samples)	Weight Loss Factor*	DDT (mg/wet kg) uncooked	DDT (mg/wet kg) pan fried	DDT (mg/wet kg) pan fried** normalized	PCB (mg/wet kg) uncooked	PCB (mg/wet kg) pan fried	PCB (mg/wet kg) pan fried** normalized
				SANTA MONICA BAY			
1 (8)	27.8	0.202	0.247	0.069	0.146	0.190	0.053
2 (6)	35.7	0.167	0.184	0.066	0.069	0.098	0.035
3 (9)	35.2	1.110	0.844	0.297	0.334	0.256	0.090
4 (7)	33.2	1.070	0.531	0.176	0.225	0.366	0.122
5 (8)	31.8	0.410	0.506	0.161	0.243	0.164	0.052
Mean ± SE	32.7	0.57±0.20	0.46±0.12	0.15±0.04	0.20±0.04	0.21±0.04	0.07±0.016
Mean % loss due to frying				74			65
				ORANGE COUNTY			
1 (4)	33.6	0.049	0.254	0.085	0.017	0.045	0.015
2 (6)	34.0	0.110	0.127	0.043	0.016	0.035	0.012
3 (4)	44.0	0.110	0.075	0.033	0.009	0.016	0.007
4 (3)	38.0	0.156	0.287	0.109	0.027	0.039	0.015
5 (6)	38.1	0.273	0.410	0.156	0.023	0.044	0.017
Mean ± SE		0.14±0.04	0.23±0.05	0.085±0.022	0.018±0.003	0.036±0.005	0.013±0.002
Mean % loss due to frying				39			28

*Calculated by estimating the % weight loss due to frying and subtracting from 100.
**Normalized to uncooked weight using the weight loss factor, i.e. pan fried concentration x weight loss factor ÷ 100.

Santa Monica Bay were four times higher than those found in croaker taken from Orange County. Total PCB concentrations were eleven times higher at Santa Monica Bay versus Orange County while after frying these differences were reduced approximately two-fold for both DDT and PCB. These two fishing sites had been selected because of this wide variation of total pollutant concentartions and we anticipated there might be a difference between effect seen with relatively high versus low tissue concentrations.

Table 2. Percent dry and lipid/wet weight of white croaker (Genyonemus lineatus) fillets uncooked and pan fried.

Composite no.	Uncooked		Pan fried	
	% dry	% lipid	% dry	% lipid
		SANTA MONICA BAY		
1	22.6	1.14	75.3	18.1
2	22.9	1.22	73.3	19.6
3	26.7	1.12	76.4	18.6
4	23.0	1.61	86.5	20.6
5	22.5	1.11	82.0	18.6
Mean	23.5	1.24	78.7	19.1
		ORANGE COUNTY		
1	21.6	0.88	88.7	28.1
2	20.8	0.87	82.4	19.4
3	21.6	0.94	58.7	15.4
4	21.4	0.90	69.0	16.9
5	21.3	0.87	68.1	14.9
Mean	21.3	0.89	73.4	18.9

Reduction of DDT and PCB concentrations could be attributed to the partitioning of these compounds from fish tissue into cooking oil while frying; both compounds are much more soluble in lipid than aqueous solvents. In all cases frying time, temperature and volume of cooking oil were constant. However, there was considerable loss of water during frying and an increase in lipid content (Table 2). The increase in lipid content may be due to absorption of cooking oil. In this portion of the study we found that cooking oil

had a detrimental effect on GC column packing material. Early analysis of oil, however (prior to obvious column degradation), indicated a lack of chlorinated hdyrocarbons (CHCs) in unused cooking oil and low levels of CHCs in used cooking oil. These levels could neither be accurately qualified nor quantified. Since the temperature used in GC analysis is comparable to the oil temperature used to fry the samples, breakdown was eliminated as a possible reason for reduced levels of CHCs.

Detectable BaP is also likely to be a function of cooking time and temperature. BaP is usually a product of incomplete combustion (NATIONAL ACADEMY OF SCIENCES 1972) and is most often associated with broiling and grilling of foods (FRITZ 1973; LIJINSKY & SHUBIK 1964; NAGAO et al. 1977). A temperature of 190°C and frying time of 4 min per side was probably insufficient to form BaP although KRONE & IWAOKA (1981) have reported formation of mutagens when sole or snapper fillets were fried in this manner. Temperature higher than 190°C was not used in this study because we were duplicating pan frying of fish as reported by sportfishermen. Temperatures greater than 190°C tend to char fish, making them less palatable.

In general, pan frying markedly reduced concentrations of total DDT and PCB in white croaker fillets. These findings are in agreement with REINERT et al. (1972) who reported that broiling and frying reduced DDT concentrations in lake trout by 64-72% and with ZABIK et al. (1979) who reported significant reductions of xenobiotics during cooking of fat trout. Fat content of fish appears to be related to reduction of contaminants during cooking (SMITH et al. 1973; WANDERSTOCK et al. 1971; ZABIK et al. 1982). The lipid content of uncooked white croaker may in part account for reduction of PCB and DDT by frying. Future considerations regarding the consumption rates of these compounds as a result of eating contaminated fish should take into consideration the effects of cooking. Further studies should also be conducted to determine the effects of cooking time, temperatures and use and volume of cooking oil on the degree to which DDT and PCB content is altered. Finally, an effort should be made to identify and quantify the degree to which these compounds are partitioned into cooking oils.

Acknowledgements - This study was supported by EPA grant #R807120010. We thank K. Hill, V. Raco, J. Alfafara and R. Arthur Jr. for technical assistance and grant administrators Robert Brice and Don Baumgartner for their expert counsel.

REFERENCES

BASCOM, W.: In: Southern California Coastal Water Research Project Biennial Report, Long Beach, California, pp. 197-210 (1980).

BLIGH, E.G., and W.J. DYER: Can. J. Biochem. Physiol. 37, 911 (1959).

DUNN, B.P.: Environ. Sci. Technol. 10, 1018 (1976).

EIS/EIR - Final Report: In: Assessment of public helath concerns associated with trace organics in seafood. Sludge management program for the Los Angeles/Orange County Metropolitan Area. Report #E7-E32, Los Angeles, California (1980).

FABIAN, B.: Arch. Hgg. Bakteriol. 152, 251 (1968).

FRITZ, W.: Dtsch. Lebenson Rundsch. 69, 119 (1973).

GOSSETT, R.W., D.A. BROWN, and D.R. YOUNG: In: Southern California Coastal Water Research Project Biennial Report, Long Beach, California, in press (1982a).

GOSSETT, R.W., H.W. PUFFER, R.H. ARTHUR, JR. , and D.R. YOUNG: Mar. Pollut. Bull. in press (1982b).

GOUGH, T.A., K.S. WEBB, and R.F. COLEMAN: Nature, Lond. 272, 161 (1978).

HUANG, D.P., J.H.C. HO, K.S. WEBB, B.J. WOOD and T.A. GOUGH: Fed. Cosmet. Toxicol. 19, 167 (1981).

KASAI, H., S. NISHIMURA, M. NAGAO, Y. TAKAHASI, and T. SUGIMURA: Cancer Lett. 7, 343 (1979).

KRONE, C.A., and W.T. IWAOKA: Cancer Lett. 14, 93 (1981).

LIJINSKY, W., and P. SHUBIK: Science 145, 54 (1964).

LIJINSKY, W., and P. SHUBIK: Indust. Med. and Surg. 2, 152 (1965).

LIU-HU, T.C., R.W. GOSSETT and D.R. YOUNG: In: Southern California Coastal Water Research Project Biennial Report, Long Beach, California. pp. 131-138 (1980).

NAGAO, M., M. HONDA, Y. SEINO, T. YAHAGI, and T. SUGIMARA: Cancer Lett. 2, 221 (1977).

NATIONAL ACADEMY OF SCIENCES: In: Particulate Polycyclic Organic Matter, Washington, District of Columbia. pp. 361 (1972).

PARIZA, M., S.H. ASHBOOR, F.S. CHU, and D.B. LUND: Cancer Lett. 7, 63 (1979).

PUFFER, H.W., S.P. AZEN, and M.J. DUDA: N. Am. J. Fisheries Mgt. 2, 74 (1982).

REINERT, R.E., P. STEWART, and H.L. SEAGRAN: J. Fish. Res. Bd. Canada 29, 525 (1972).

SMITH, W.E., K. FUNK, and M.E. ZABIK: J. Fish. Res. Bd. Canada 30, 703 (1973).

SMOKLER, P.E., D.R. YOUNG, and K.L. GARD. Mar. Pollut. Bull. 10, 331 (1979).

WANDERSTOCK, J.J., W.W. ISKAT, W.H. GUTENMANN, and D.J. LISK: N.Y. Fish Game J. 18, 70 (1971).

WINE, V.: In: Southern California independent sportfishing survey, Annual report #3, July 1, 1977 to June 30, 1978. Marine Resources Region, California Department ofFish and Game, Administrative Report #79-3 (1979).

YAMAIZUMI, Z.. T. SHIOMI, H. KASAI, S. NISHIMURA, Y. TAKAHASHI, M. NAGAO, and T. SUGIMURA: Cancer Lett. 9, 75 (1980).

YOUNG, D.R., T.C. HEESEN, and R.W. GOSSETT: In: Environmental Impact and Health Effects Volume 3. Ann Arbor, Michigan, pp. 471-485 (1980).

ZABIK, M.E., P. HOOJJAT, and C.M. WEAVER: Bull. Environ. Contam. Toxicol. 21, 136 (1979).

ZABIK, M.E., C. MERRILL, and M.J. ZABIK: Bull. Environ. Contam. Toxicol. 28, 710 (1982).