PCBs, Dioxin-like PCBs, and Organochlorine Pesticides in Farmed Atlantic Salmon (Salmo salar) from Maine and Eastern Canada

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Introduction

Between 1987 and 2000, salmon consumption in the United States increased by more than 26% annually, and by 2000, more than half of the salmon consumed was farmed.[1] An estimated 23.1 million US residents eat salmon more often than once a month, 1.3 million eat salmon at least once a week, and 180,000 eat salmon more often than twice a week.[2] In Maine, the industry tripled production between 1990 and 2000[3], and now supplies ~18% of US domestic consumption of farmed salmon. Virtually 100% of Maine farmed salmon is marketed in New England along with farmed salmon from Canada and Chile. Recently, organically grown salmon from Norway has also been marketed at higher prices to consumers in this region.

Recent studies have shown that concentrations of PCBs, dioxins, and other persistent organic pollutants (POPs) can be significantly higher in farm-raised salmon than in wild salmon[4,5], and concentrations in farmed salmon from Europe are generally higher than those in farmed salmon from North America. In the US, the possible contribution of toxic POPs to human body burdens resulting from the trend of increasing farmed salmon consumption could clearly be of concern for heavy consumers. Here we provide results on the analysis of PCBs, dioxin-like PCBs, and organochlorine pesticides in farmed and wild salmon marketed to consumers in the northeast region, including farmed Atlantic salmon *(Salmo salar*) from Maine and eastern Canada, organically farmed salmon from Norway, and wild Chinook salmon (*Oncorhynchus tshawytscha)* from Alaska. Whereas contaminant loads in farmed salmon have been broadly compared across regions, this study examined possible intra-regional differences in POP concentrations in salmon from individual producers. In addition, most studies report POP concentrations in skin-on samples because farmed salmon is mainly sold to consumers with skin-on. Since lipophilic contaminants are stored in fat, removal of skin would be expected to reduce contaminant levels in the consumed portion of fish. Thus, we analyzed skin-on and skin-off samples to determine to what extent the presence of skin may contribute to contaminant loads.

Methods and Materials

Samples. A total of 70 farmed and wild salmon were collected from wholesale and retail outlets in Maine between August 2003 and May 2004. The farmed salmon represented six farming locations in three regions, including two farms in eastern Maine, three in eastern Canada, and an organic farm in Norway. Wild Chinook salmon from Alaska were also purchased from a wholesale supplier in Maine. Suppliers provided information on the origin (region and farm) of the fish. Ten whole fish were obtained from each farm, nine of which were randomly pooled into three composite samples of three fish each. The whole fish were thawed, weighed, measured, filleted and deboned to yield two fillets per fish, one with skin on and one with skin removed. The fillets from three fish were then homogenized in a high speed processor to make two composites (skin-on/off), resulting in a total of 42 composite samples (21 skin-on samples, 21 skin-off samples) for analysis. Samples were subdivided into smaller replicate portions of 100g, and frozen at -20° C. in borosilicate glass containers with PTFE-lined lids. The samples were sent packed on ice or frozen gel-packs to the Wadsworth Center, NY State Department of Health, Albany, NY, where they were stored at -20° C. prior to analysis.

Analytical Methods. Samples were analyzed for PCDD/Fs, PCBs (including dioxin-like PCB congeners), and OC pesticides according to methods described in detail previously[6] with modifications. Briefly fifteen to twenty grams of wet weight tissue were taken from each composite sample and homogenized with granular sodium sulfate and Soxhlet extracted for six hours. The extract was concentrated and lipid content was determined gravimetrically. After addition of ^{13}C-labeled internal standards, the extract was cleaned up by gel permeation chromatography (GPC) and then on a multilayer silica gel column and injected into a GC (Hewlett-Packard 6890) coupled with a mass selective detector (Hewlett-Packed, series 5973). Chromatographic separation of PCB congeners was achieved on a DB-5MS capillary column. Pesticides were quantified by GC-ECD after fractionation of another portion of the extract on a Florisil column. Quantification of 2,3,7,8-substituted PCDD/F congeners and non-ortho coplanar PCB congeners was carried out using a high resolution GC coupled with a high resolution MS (HRGC-HRMS; HP 6890GC with JEOL JMS-700D HRMS). PCDDs/Fs with 4-6 chlorines were separated and quantified on an SP-2331 column, while PCDDs/Fs with 7-8 chlorines and non-ortho PCBs were separated on a DB-17 column.

Determination included: 45 PCB congeners, including 4 non-ortho PCB congeners (IUPAC nos. 77, 81, 126, 169) and 3 mono-ortho PCB congeners (105, 118, 189); 17 PCDD/Fs, and 11 OC pesticide isomers (DDTs: p,p'-DDE, p,p'-DDD+o,p-DDT, p,p'-DDT; CHLs: trans-nonachlor, cis-chlordane, oxychlordane, cis-nonachlor, trans-chlordane; HCHs: a-HCH, b+g-HCH; and HCB). In the majority of samples (>60%), concentrations of PCDD/F congeners and the non-ortho PCB congener 81were below the limits of detection; these congeners were reported as NDs. TEQs for 6 dioxin-like PCBs (77, 126, 169, 105, 118, and 189) were calculated using WHO-TEFs.[7] For these dioxin-like PCBs, results are given as sum of the PCB WHO-TEQ. Contaminant concentrations in skin-on samples were used for comparisons with other studies.

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Results and Discussion

The results of this study were comparable and of a similar order of magnitude as those recently reported elsewhere.[4,5,8,9] PCB concentrations in farmed salmon (as a group) were significantly higher than those in wild salmon (p=0.012), with skin-on values ranging from 3.8 - 8.1 ng/g, wet weight in the wild samples and 7.2 - 29.5 ng/g, wet weight in the farmed samples. Compared by region of origin, POP concentrations in Maine and Canadian salmon were similar, but significant differences were found in concentrations of PCBs, DDT, and HCHs between the Norwegian samples, Maine and Canadian samples (as a group), and the Alaskan wild samples (Fig. 1a). The highest POP concentrations were found in organically grown salmon from Norway, with the exception of hexachlorocyclohexanes (HCHs), which were lowest in the Norwegian samples. Wild-caught Alaskan salmon had the lowest concentrations of POPs with the exceptions that HCH concentrations in the wild salmon exceeded those in the samples from Norway, and hexachlorobenzene (HCB) concentrations were higher in the wild salmon than in the farmed salmon from Maine and Canada.

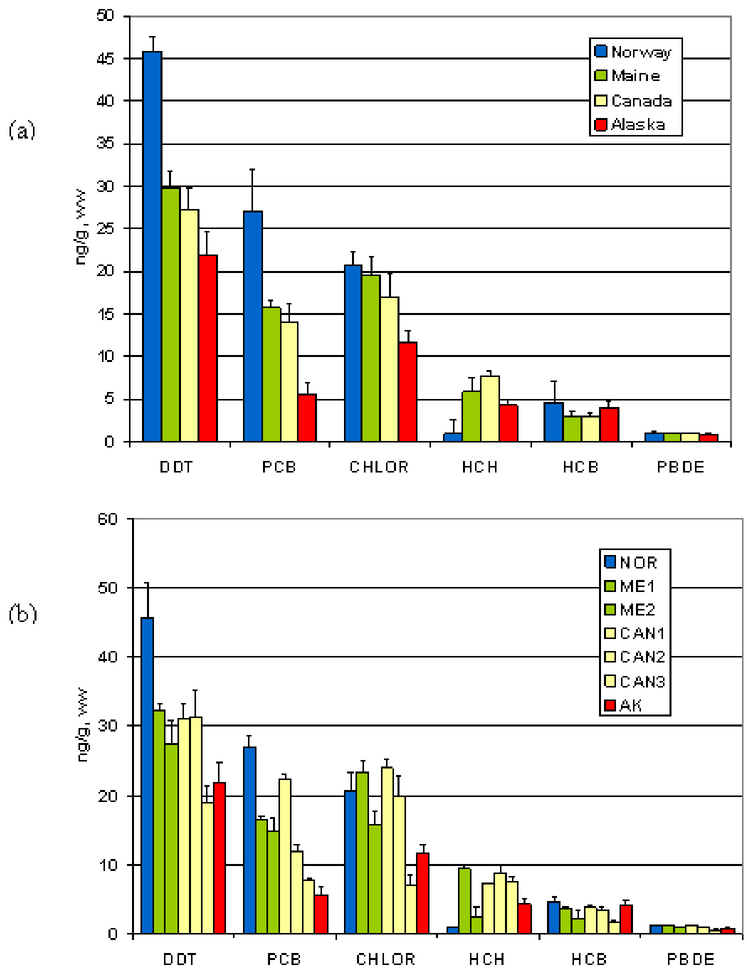

Fig. 1. POP concentrations (in ng/g, wet weight) in skin-on salmon samples (a) by region and (b) by producer

However, as Fig. 1b illustrates, contaminant distributions were highly variable among individual producers, and between individual producers and wild-caught salmon. PCB and DDT concentrations were highest in the organically grown Norwegian farmed salmon, ranging from 23.7 - 29.5 ng/g, ww for PCBs and 36.3 - 53.3 ng/g, ww for DDT, while chlordanes (CHLs) and HCHs were highest in salmon from one Maine and one Canadian farm. PCB concentrations were lowest in the Alaskan wild salmon (3.8 - 8.1 ng/g, ww), but DDT and CHL concentrations were lowest in salmon from a Canadian farm. Interestingly, the highest and lowest CHL concentrations were found in salmon from two Canadian farms that use commercial feed from the same supplier, which could reflect batch variation in the feed. The HCH concentrations found in the Norwegian salmon were an order of magnitude lower than those in farmed salmon from regional producers and the wild salmon, reflecting lower HCH contamination in forage fish used in the organic feed.

Lipid content (%) varied significantly in salmon from the different producers [$F=23.7$, $p<0.001$, df $=6,14$]. Lipids were highest in the organically grown Norwegian salmon (18.4%) and salmon from one Maine farm (18.2%), while wild Alaskan samples had the lowest lipid content (7.6%), reflecting differences in diet between wild and farmed fish. The aquaculture industry favors diets high in marine fish oils (30-36%), and these oils may contribute substantially to the contamination of farmed salmon by lipophilicPOPs. The Norwegian bioculture salmon diet was lower in fish oil content (a stated maximum 28% of the total diet), and claimed to be "virtually free of dioxins and PCB trace elements" based on quantification of ICES7 PCBs in 11 composite samples.[10] Interestingly, this study found that the Norwegian samples were not only the highest in fat content but their mean PCB burdens (27 ng/g, ww) were highest among the individual producers and more than three times higher than the company's reported concentrations (8 ng/g, ww) for the sum of ICES7 PCBs.

Table 1 shows the concentrations of dioxin-like PCBs (given as PCB WHO-TEQ) in salmon samples with and without skin by region. The main constituent within the dioxin-like PCB congeners was penta-CB 126, contributing 64-86% to the total PCB WHO-TEQ values, which ranged in skin-on samples from the lowest TEQ of 0.16 pg/g, ww in the wild Alaskan samples to the highest value of 2.85 pg/g, ww in the organically grown salmon from Norway. Compared by region, WHO-TEQs of dioxin-like PCBs in the Norwegian samples were an order of magnitude higher than those in farmed salmon from Maine and eastern Canada, which ranged from a mean of 0.66 to 0.57 pg/g, ww.

Table 1. WHO-TEQ values (in pg/g, wet weight) of dioxin-like PCBs in salmon by region

Region	**Skin**	**Fat Content**	**PCB 77**	**PCB 81**	**PCB 126**	**PCB 169**	**PCB 105**	**PCB 118**	**PCB 189**	**∑PCB-WHO-TEQ**

		(%)								
Norway	Skin-on	18.37	0.0043	ND	2.4443	0.1253	0.0341	0.1220	0.1203	2.8503
(organic)	Skin-off	15.15	0.0012	ND	0.5673	0.0251	0.0374	0.1173	0.1118	0.8601
Maine	Skin-on	12.94	0.0011	ND	0.4757	0.0156	0.0236	0.0672	0.0737	0.6568
(farmed)	Skin-off	10.30	0.0009	ND	0.3542	0.0108	0.0196	0.0546	0.0528	0.4930
Canada	Skin-on	13.57	0.0008	ND	0.4124	0.0102	0.0209	0.0644	0.0613	0.5700
(farmed)	Skin-off	12.14	0.0011	ND	0.4816	0.0118	0.0163	0.0476	0.0488	0.6073
Alaska	Skin-on	7.61	0.0003	ND	0.1126	ND	0.0042	0.0231	0.0194	0.1645
(wild)	Skin-off	5.51	0.0003	ND	ND	ND	0.0040	0.0126	0.0135	0.0853

ND=not detected

Intra-producer differences were also highly significant, with mean TEQs ranging from 0.49 to 0.7 pg/g, ww, in salmon from the two Maine and three Canadian farms (Table 2). These values are at the lower end of WHO-TEQs recently reported in farmed salmon from eastern Canada[4], while the TEQs of the Norwegian bioculture samples are higher than those recently reported in organically farmed salmon from Ireland[11] and conventional farmed salmon from Norway.[4] It should be pointed out that our TEQ values were derived from only 7 of the 12 dioxin-like PCBs (IUPAC nos. 77, 81, 126, 169, 105, 118, and 189), and did not include TEQs of 6 mono-ortho PCBs, PCDDs, or PCDFs. Dioxin-like PCBs typically dominate the WHO-TEQ in salmon, contributing 70-80% to the total, thus, it is likely that the TEQs reported here underestimate the total WHO-TEQ in these samples by about 30%.

Table 2. WHO-TEQ values (in pg/g, wet weight) of dioxin-like PCBs in salmon by producer

Producer	**Skin**	**Fat Content (%)**	**PCB 77**	**PCB 81**	**PCB 126**	**PCB 169**	**PCB 105**	**PCB 118**	**PCB 189**	**∑PCB WHO-TEQ**
NOR	Skin-on	18.37	0.0043	ND	2.4443	0.1253	0.0341	0.1220	0.1203	2.8503
	Skin-off	15.15	0.0012	ND	0.5673	0.0251	0.0374	0.1173	0.1118	0.8601
ME1	Skin-on	18.21	0.0013	ND	0.5066	0.0109	0.0270	0.0729	0.0830	0.7016
	Skin-off	15.20	0.0014	ND	0.5250	0.0135	0.0238	0.0665	0.0598	0.6900
ME2	Skin-on	7.66	0.0009	ND	0.4448	0.0203	0.0202	0.0615	0.0644	0.6121
	Skin-off	5.39	0.0004	ND	0.1834	0.0081	0.0154	0.0427	0.0458	0.2960
CAN1	Skin-on	12.51	0.0009	ND	0.4475	0.0141	0.0331	0.1044	0.1008	0.7009
	Skin-off	11.81	0.0013	ND	0.5697	0.0166	0.0185	0.0614	0.0550	0.7226
CAN2	Skin-on	14.25	0.0008	ND ND	0.3494	0.0080	0.0182	0.0578	0.0526	0.4868

	Skin-off	11.34	0.0098		0.4257	0.0110	0.0182	0.0487	0.0566	0.5611
CAN3	Skin-on	13.94	0.0007	ND ND	0.4402	0.0085	0.0112	0.0309	0.0306	0.5222
	Skin-off	13.27	0.0098		0.4494	0.0079	0.0122	0.0328	0.0349	0.5381
AK	Skin-on	7.61	0.0003	ND ND	0.1126	ND	0.0042	0.0231	0.0194	0.1645
	Skin-off	5.51	0.0003		ND	ND	0.0040	0.0126	0.0135	0.0853

ND=not detected

This study examined the possible benefit to the consumer of skin removal by lowering fat content and thus PCB-dioxin TEQs in the consumable portion of the fish. When comparing levels in wild and farmed salmon (as a group), there appeared to be both a substantial reduction in fat (by 16-28%) and a lowering of PCB WHO-TEQs (by 38-48%) in the skin-off samples. However, as Table 2 illustrates, when samples from individual producers were compared, skin removal resulted in a variable reduction in fat content in salmon samples, ranging from only a small reduction of 5-6% fat in fish from two Canadian farms to a substantial reduction of 28% fat in wild salmon from Alaska, and 30% fat in fish from one Maine farm. Moreover, skin removal did not consistently result in a reduction of PCB WHO-TEQs in these samples. Whereas total TEQs were lower by a factor of 3.3 in the Norwegian skin-off samples, and almost two-fold lower in the skin-off Alaskan wild samples, TEQs were actually slightly higher in the skin-off samples from the three Canadian farms and nearly identical in skin-on and skin-off samples from a Maine farm. Thus, in contrast with results of a recent study of Irish farmed salmon[11], this study did not find that the removal of skin from farmed salmon confers clear health benefits to the consumer.

The importance of labeling salmon as farmed and identifying the region of origin has been emphasized as a means to helping the consumer avoid unnecessary exposure to highly contaminated fish. However, given the significant intra-regional and intra-producer variations in contaminant concentrations found in this study, it appears that the consumer's ability to minimize exposure to contaminated farmed salmon through such labeling may be limited, and restricted consumption may be the only means of protecting public health. In this study, the highest concentrations of PCBs, dioxin-like PCBs, and DDT were found in the organically farmed salmon from Norway, which raises additional issues for the consumer, particularly since the PCB concentrations in these samples were three times higher than the ICES7 PCB levels reported by the producer. In contrast with findings of Karl et al.[12] who found higher levels of PCB WHO-TEQs in conventional farmed salmon from Norway and Ireland than in organically farmed salmon from western Ireland, the PCB WHO-TEQs in the organically farmed salmon from Norway in this study were an order of magnitude higher than those of the conventional farmed salmon from Maine and eastern Canada, and are in the higher range of the values of 0.7 to 3 pg WHO-TEQ, ww, reported in farmed salmon from around the world.[4]

In view of the increasing availability of farmed salmon in the marketplace and the rising consumption rates among US residents, the ongoing determination of dioxin-like compounds not only in commercial feed but also in farmed fish destined for human consumption is essential for human dietary exposure assessment.

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References

1. Fisheries Global Information System (FI-GIS), United Nations Food and Agriculture Organization (2004) Available at: www.fao.org/fi/statist/statist.asp.

2. Redmayne, P. (2000) *SeaFood Business*. August 2000.

3. Gardner Pinfold (2003) Report to the ME Department of Marine Resources. Gardner Pinfold Consulting

Economists, Ltd., 84 pp.

4. Hites, R. A., Foran, J. A., Carpenter, D.O., Hamilton, M. C., Knuth, B. A., and Schwager, S. J. (2004) *Science* 303:226-229.

5. Jacobs, M., Covaci A., and Schepens, P. (2002) *Environ. Sci. Tech*. 36:2797-2805.

6. Kannan, K., Kajiwara, N., Le Boeuf, B.J. and Tanabe, S. (2004) *Environ.Poll*. 131:425-434.

7. Van den Berg, M., Birnbaum, L., et.al. (1998) *Environ.Health.Persp*. 106:775-792.

8. Zuccato, E., Fanelli, R., Fattore, E., and Valdicelli, L. (2004) *Organohalogen Compounds* 66:1968-1973.

9. Easton, M.D.L., Luszniak, D., and Von der Geest, E. (2002) *Chemosphere* 46:1053-1074.

10. Norway Directorate of Fisheries (2003) Statement concerning PCB in farmed fish. PCB-erklaering, oppdrettsfisk, engelsk, 2001/04.

11. Gruemping, R., Hamm, S., Stegemann, D, and Maulshagen, A. (2004) *Organohalogen Compounds* 66:1947-1954.

12. Karl, H., Ruoff, U., Schwind, K-H., and Jira, W. (2004) *Organohalogen Compounds* 66:1661-1667.