PBDE AND PCB LEVELS CORRELATED IN WILD CAUGHT AND FARM-RAISED FISH FILLETS IN THE USA

Douglas Hayward[1], Jon Wong[1], Alexander Krynitsky[1]

[1]US Food and Drug Administration College Park

Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are two classes of industrial chemicals that have been widely used in the manufacture of many materials found commonly in highly industrial societies. PCBs used as an electrical insulator and in plastics have been banned in the US since 1977. PCB levels have steadily declined in foods. PBDEs are currently used as effective flame retardant in electronics, automobiles, home furnishings, textiles and in building materials[1]. Environmental levels have not reached equilibrium. Both classes are ubiquitous contaminants with a strong tendency for bioaccumulation. The detection of PBDEs in human and some animal fats and fish/shellfish has been reported[1]. Recent reports of PBDEs in the US population have reported PBDE levels higher than most other industrialized countries[2]. The pathway of these exposures is not precisely known, but one likely pathway is food. One report from the US[3] revealed very high levels from multiple point sources (>1000 ng/g lipid) in freshwater sportfish collected in the Roanoke/Dan River basin of southern Virginia. Reported levels in commercial foods have been relatively scarce until very recently for any country in the world especially the US. Reports available from limited samplings of fish and other foods in Spain, Germany and Japan show wide variations in levels of PBDE congeners, but very similar congener profiles[4-7]. For example, Bocio et al. composited 10 samples of bluefish from five locations reporting one result for bluefish of 1ng/g. One study involving 22 samples of fish collected in San Francisco Bay found relatively high levels of PBDEs with BDE 47 approaching the level of PCB 153[8] as was observed in the freshwater fish from Virginia rivers with higher levels[3]. A predictable correlation was found in this cross-sectional sampling of fish from this one area[8]. The ratio or the slope between the classes of persistent compounds in fish species could indicate trends for contamination in a given area providing useful information for environmental management[3,12].

US FDA is planning to monitor some PBDE congeners beginning 2005. Data collection will begin with fish and shellfish and most likely be expanded to other foods. Fish/shellfish are already being monitored for PCDD/F and some PCB content. Several different instrumental approaches have been used successfully to measure PBDEs in human tissues and in environmental media including HRGC/HRMS, ECNI-LRMS, EI-LRMS and tandem mass spectrometry[9]. The focus of this study is to determine PBDE levels in fish that are already known to have higher levels of PCBs relative to other fish or other foods. EI-LRMS was selected for initial testing with PBDE measurements in fish for its simplicity and availability in every FDA field laboratory.

Methods

Bluefish, "rockfish", wild caught Alaskan King and Coho salmon and farm-raised Atlantic salmon fillets were collected from four markets located in either Maryland or Washington, DC. One bluefish and one "rockfish" were collected as whole fish and filleted. "rockfish" is a common name often used to refer to any one of up to 300 different species of fish. The "rockfish" label used here commercially probably refers to *Morone saxatilis* or striped bass, a local species that inhabits both fresh and salt water. A single bluefish sample was collected as part of FDA's routine PCDD/F monitoring program in North Carolina, representing a composite of 12 commercial fillets. A total of four individual farm-raised Salmon and four wild caught (as identified in retail market) salmon along with three bluefish and four "rockfish" fillets were collected as fillets. All fillets were homogenous with the skin removed.

All samples were determined using 10g wet weight portion of the homogenized skinned fillet with the exception of bluefish collected in North Carolina (5g wet weight). All test portions were fortified with $^{13}C_{12}$-PCBs 28, 52, 77, 101, 105, 114, 118, 126, 138, 153, 156, 157, 167, 169, 170, 180, 189 and BDEs 3, 15, 28, 47, 99, 153, 154, 183, 197, 207 and 209. PCBs targeted for analysis were PCB 28, 37, 44, 49, 52, 66, 74, 77, 95, 99, 101, 105, 110, 114, 118, 126, 137, 138, 153, 156, 157, 167, 169, 170, 180, 187 and for BDEs; 28, 47, 49, 66, 71, 77, 99, 100, 119, 153 and 154. Test portions were extracted as previously described[10]. All fish samples were clean up over basic/acid and neutral silica gel 60 column. Some samples with lower levels of PBDEs or higher noise were clean up over Woelm neutral alumina or ICN Super I basic alumina. PCBs were measured using a Saturn 4D ion trap in tandem MS mode[10] while PBDEs were measured with an Agilent 5793 GC/MS in electron impact selected ion monitoring (SIMs) mode equipped with a 20M DB-XLB mini-bore (0.18 mm) column. Recoveries for labeled standards were between 75-100%.

Results and Discussion

Twenty-five of 27 targeted PCB congeners were found in all samples. PCBs 126 and 169 were analyzed with the PCDD/Fs for some samples through a separate PCDD/F containing fraction[11]. PBDEs 28, 47, 99 and 100 were found in all samples, except the lowest Coho salmon, while BDE 154 and 153 were found in most "rockfish" and bluefish samples. BDE-154 was found only in Icelandic and Atlantic salmon and BDE 153 in one Atlantic salmon due to higher LODs for these congeners and lower expected levels. The highest samples were the bluefish for both PCBs and PBDEs, although one sample was lower than all "rockfish" samples (table 1). A single bluefish sample had the highest levels for PCBs (0.8mg/kg) and PBDEs (0.036mg/kg) (table 1). Wild caught Alaskan Coho salmon were the lowest for PCBs as has been reported recently[12], and contained as little as 34pg/g BDE 47. Alaskan King salmon were closer to farmed-raised levels. BDE 47 was 59-63% of the total PBDEs in all fish. PCB 153 and BDE 47 levels correlate strongly (figure 1) with a correlation coefficient of 0.94 when all species are combined. When separated by species the relationship is still significant with bluefish 0.92 and salmon, 0.85 (figure 2&3). The slope of the linear regression for PCB 153 and BDE 47 in bluefish was 7.5 and 2.7 for "rockfish", while all salmon species gave a much lower slope of 2.0 (figures 2&3). From this limited data, it appears that the wild caught and farm-raised salmon will have different slopes as well. The PBDE levels found in bluefish and "rockfish" are higher than previously reported in commercially collected finfish[4,5].

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Table 1. Wild caught salmon, rockfish, bluefish and farm-raised Atlantic salmon levels for PBDEs and PCBs in ng/g wet weight.

	PCBs[a](RPD)	PBDEs(RPD)[b]	Ratio (PCB/BDE)
Wild Alaskan King salmon (MD)[c]	5.8	0.71	8
Wild Alaskan King salmon (DC)	5.4	1.2	4.5
Wild Alaskan Coho salmon (MD)	0.35	0.04	9
Wild Alaskan Coho salmon (MD)	2.9	0.24	12
Farmed Atlantic salmon (DC)	1.8(3)	0.21(1)	8.6
Farmed Atlantic salmon (MD)	12	1.2	10
Farmed Atlantic salmon (MD)	12	1.5	8
Farmed Icelandic salmon (MD)	8.0	0.49	16
Rockfish (DC)	22(11)	1.7(7)	13
Rockfish (MD)	35	3.7	10
Rockfish (MD)	39	2.3	18
Rockfish (DC)	93	7.2	13
Rockfish (MD)	120	14	9
Bluefish (NC)	800(26)	36(16)	22
Bluefish (DC)	140(5.9)	6.5(0.7)	22
Bluefish (MD)	106	7.4	14
Bluefish (MD)	12	0.61	20
Bluefish (MD)	280	24	12

[a]Sum of 25 PCB congeners.
[b]RPD = relative percent difference from the mean of duplicate analyses.
[c]Region where fish was purchased; DC=Washington, DC, MD=Maryland, NC=North Carolina.

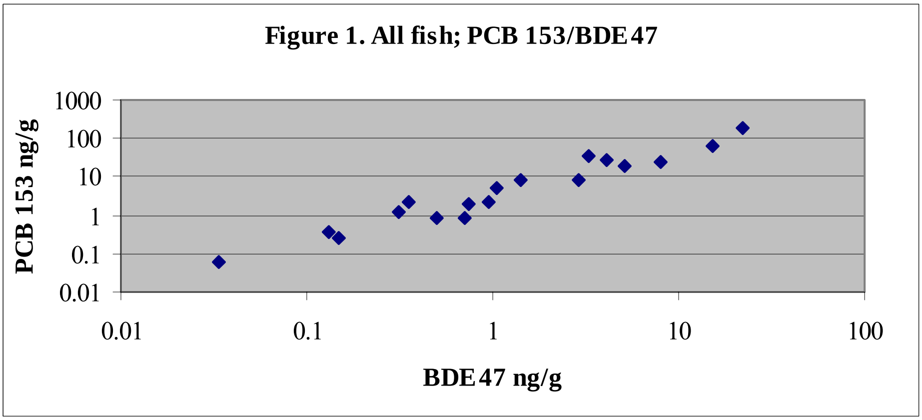
Figure 1. All fish; PCB 153/BDE 47
PCB 153 ng/g
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
BDE 47 ng/g

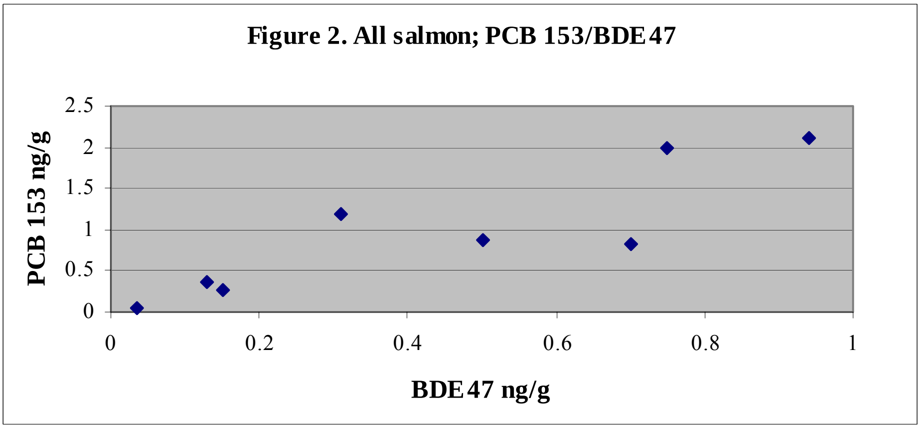
Figure 2. All salmon; PCB 153/BDE 47
PCB 153 ng/g
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
BDE 47 ng/g

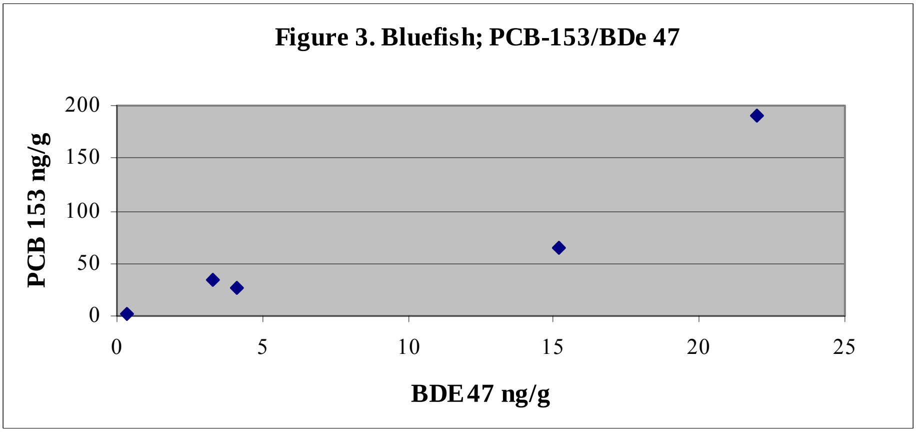
Figure 3. Bluefish; PCB-153/BDe 47
PCB 153 ng/g
200
150
100
50
0
0
5
10
15
20
25
BDE 47 ng/g