COMPARISON OF THE LEVELS FOR PCDD/FS AND 28 PCB CONGENERS IN FINFISH FROM LAKE CHARDARA, KAZAKHKSTAN AND WASHINGTON, DC

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Introduction

A comprehensive survey, begun in 1994, of persistent organochlorine pollutants in the former Soviet Republic of Kazakhstan revealed elevated levels of a few chemicals including 2,3,7,8-TCDD[1]. The unusual TCDD levels (and PeCDD) were highest in breast milk samples collected in an agricultural region of Southern Kazakhstan, with maximal levels found in samples from donors residing in State farms next to Lake Chardara[2]. Unusually elevated TCDD contamination was also found in animal-based foods from State Farms near Lake Chardara[2]. Although these early investigations found wide-spread TCDD-contamination in animal foods, with levels >10-fold higher than US levels, the amounts of meat and dairy consumed did not fully account for the observed elevated body burdens in the rural areas near Lake Chardara[2]. Fish from Lake Chardara are an important source of protein for some people in this region and a possible source of TCDD contaminants. This study measured TCDD levels in fish from Lake Chardara to determine their contribution to the body burden. An earlier study assessed the PCB congener profile in breast milk from the region. The current study measured PCB congeners in the fish to assess the contribution of fish consumption to POPs body burdens in rural Kazakhstan.

Methods

During the summer of 2000, sections of whole fish from five species commonly found in Lake Chardara were collected after being cleaned, but not filleted. The common names were carp, bream, pike, Kapacb (Crucian in Kazakh) and Krachonëpka. The sections were immediately frozen and transported to the laboratory and kept at -40^{o}C until analysis. Three species of wild caught and aquaculture finfish were collected from a Washington, DC area market for purposes of comparison. In 2001, Atlantic salmon, bluefish, and "Rockfish" were collected as fillets. These fish species have been recently sampled extensively by FDA throughout the US for PCDD/Fs[4].

Test portions were prepared as previously described[5]. The test portions were fortified with 100 pg, 250 pg and 1000 pg of 15 $^{13}C_{12}$-PCDD/Fs, PCBs 77, 126 and 169 and PCBs 28, 52, 101, 105, 114, 118, 138, 153, 156, 157, 167, 180, 189 respectively. PCDD/Fs and PCBs 77, 81, 126 and 169 were measured with a Saturn 2000 quadrupole ion trap in tandem MS mode. PCBs 28, 37, 44, 49, 52, 66, 74, 95, 99, 101, 105 110, 114, 118, 137, 138, 149, 153, 156, 157, 167 170, 180, 187 were determined using a Saturn 4D quadrupole ion trap operated in tandem MS mode. Both instruments were optimized for either the formation of M-COCl (PCDD/Fs) or M-2Cl (PCBs) through a systematic examination of the parameters as discussed previously[6,7].

Results and Discussion

TCDD was not detectable in Kazakhstan fish samples. Kazakhstan fish were not above the MDL of ~0.05 pg/g (Table 1), except one sample containing 0.07 pg/g. PCBs 77 and 126 were found in all samples above 2 pg/g, but PCB 169 was below the MDL of 0.1 pg/g. Mono and di-ortho substituted PCBs were found in all samples and contained a congener profile reassembling human milk[3]. The intermittent availability of fish (none available during the fall and winter) and the failure to measure significant amounts of TCDD and PeCDD in the Kazakhstan fish makes it unlikely that finfish are the source of the elevated TCDD and PeCDD levels in persons living in rural areas of Southern Kazakhstan. Levels for TCDD found in lamb fat, cow's milk fat, butter were at least 10-fold higher (or 10-100 fold) than the levels in finfish fillet[2,5]

In the Washington, DC area fish, bluefish contained the highest levels of both dioxins and dioxin-like PCBs. TCDD, TCDF, PeCDD and 2,3,4,7,8-PeCDF were easily detected between 0.3 and 2.4 pg/g (Table 2). PCB 126 was 97 pg/g wet weight, but was also detected in Atlantic salmon and rockfish at 2.3 and 4.4 pg/g respectively. The dioxin TEQ for bluefish was only 1.8 pg/g wet weight, half the maximum allowable level of 4.0 pg/g wet weight of fish fillet. Including PCB 77, 126 and 169 raised the TEQ to 11.1 pg/g wet weight, three times the current maximum level. Clearly, some commercially caught fish species will exceed the current maximum levels when PCBs are included in the TEQ. Major mono- and di-ortho-PCB congeners were also detected in all samples (Table 2), but these congeners contributed less than 20% to the total TEQ.

Conclusions

Kazakhstan finfish from Lake Chardara did not contain any unusual TCDD or PeCDD contamination. Overall, Kazakhstan finfish TEQs were lower than TEQs in fish from Washington, DC, except for the farm-raised Atlantic salmon. All fish were below 1 pg/g total TEQ except bluefish. Congener profiles and TEQs were similar for most Washington finfish. Bluefish was the exception, with a different PCB congener profile and much higher TEQ and PCDD/F/PCB levels.

References

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Table 1: PCDD/F and PCB levels for finfish from Lake Charadara, Kazakhstan; pg/g wet wt. fillet.

(For TEQs; nondetects = ½ LOD) PeCDF2 = 2,3,4,7,8-pentachlorodibenzofuran, HxCDD2 = 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin, HxCDF2 = 1,2,3,6,7,8-hexachlorodibenzofuran, HpCDF1 = 1,2,3,4,6,7,8-heptachloro-dibenzofuran; I = interference

Common name	Pike/Perch	Carp	Bream
Congener			
TCDD	<0.05	<0.05	<0.06
PeCDD	<0.06	<0.07	<0.07
HxCDD2	<0.2	<0.2	<0.2
HpCDD	<0.3	<0.3	<0.3
OCDD	<0.5	<0.5	<0.5
TCDF	0.23	0.33	0.65
PeCDF2	<0.07	<0.06	<0.07
HxCDF2	<0.1	<0.1	<0.1
HpCDF1	I	<0.1	I
OCDF	<0.5	<0.5	<0.5
Dioxin TEQ	0.11	0.11	0.14
PCB-77	22	30	47
PCB-126	1.8	3.4	4.4
PCB-169	<0.1	<0.1	<0.1
Coplanar TEQ	0.19	0.35	0.45
PCB-28	nd	nd	307
PCB-37	nd	nd	nd
PCB-44	nd	27	57
PCB-49	16	60	140
PCB-52	35	114	280
PCB-66	38	104	340
PCB-74	23	79	230
PCB-95	18	47	80
PCB-99	32	140	240
PCB-101	39	160	270
PCB-105	25	72	145
PCB-110	6.9	27	75
PCB-114	1.7	4.9	8.9
PCB-118	57	180	360
PCB-137	5.8	24	43
PCB-138	78	260	550
PCB-149	35	70	170
PCB-153	75	213	460
PCB-156	4.8	18	26
PCB-157	1.7	3.6	7.2
PCB-167	2.8	10	16
PCB-170	7.4	20	30
PCB-180	13	45	89
PCB-187	5.5	28	38
PCB-TEQ	0.2	0.39	0.52

Table 2: PCDD/F and PCB levels for selected finfish from Washington, DC; pg/g wet weight fillet (For TEQs; nondetects = ½ LOD); I= Interference; nd= not detected

Common name	Bluefish	Rockfish	Salmon
Congener			
TCDD	0.30	<0.06	<0.05
PeCDD	0.52	<0.1	<0.06
HxCDD2	<0.1	<0.2	<0.2
HpCDD	<0.1	<0.1	<0.2
OCDD	<0.3	<0.3	<0.3
TCDF	2.4	0.21	<0.15
PeCDF2	1.3	0.14	<0.05
HxCDF2	<0.1	<0.2	<0.1
HpCDF1	<0.1	<0.2	<0.2
OCDF	<0.2	<0.3	<0.2
Dioxin TEQ	1.8(n=2)	<0.25(n=2)	<0.12(n=2)
PCB-77	105	16	9.1
PCB-81	6.8	0.8	0.25
PCB-126	92	4.4	2.3
PCB-169	6.0	0.59	0.42
Coplanar-TEQ	9.3(n=2)	0.45(n=2)	0.24(n=2)
PCB-28	800	71	60
PCB-37	5.9	nd	I
PCB-44	580	68	28
PCB-49	1900	240	39
PCB-52	2000	260	87
PCB-66	2900	310	86
PCB-74	1900	160	48
PCB-95	1700	160	49
PCB-99	9700	550	79
PCB-101	9600	680	148
PCB-105	3100	195	90
PCB-110	1100	130	32
PCB-114	140	8.9	4.0
PCB-118	13800	680	218
PCB-137	1300	200	44
PCB-138	28000	1500	250
PCB-149	8800	940	150
PCB-153	36000	2800	320
PCB-156	1100	83	23
PCB-157	300	21	4.9
PCB-167	750	200	12
PCB-170	700	130	50
PCB-180	4800	1200	126
PCB-187	7000	940	50
PCB- TEQ	11.8	0.59	0.29