POLYCHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN LEVELS AND PATTERNS IN FISH SAMPLES ANALYZED WITHIN THE SWEDISH DIOXIN SURVEY

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ABSTRACT

The lipid weight levels of PCDD/F in sixty-three fish samples have been analyzed using multivariate statistical methods (principal component analysis, SIMCA classification). The fish species represented include herring, pike, burbot, whitefish, cod, trout and Arctic char. Collection sites represent the Baltic Proper (background station), hot spots along the Swedish coast of the Bothnian Sea and Bothnian Bay, two large lakes with industries (Lakes Vänern and Vättern), one pristine mountain lake (Lake Storvindeln) and three rivers. PCDD/F patterns in pike, cod and herring taken from the same area are different from each other indicating species differences. Muscle and liver analyzed from the same individuals have similar PCDD/F levels and patterns on a lipid weight basis. PCDD/F levels and patterns in herring and pike samples are significantly different from each other and all other fish samples indicating species differences in accumulation independent of collection site. Fall and spring Baltic herring are significantly different from each other due to higher PCDD/F levels in spring herring. Both fall and spring Baltic herring are significantly different from herring collected along the Swedish coast of the Bothnian Sea based on pattern differences.

INTRODUCTION

The Swedish Environmental Protection Agency is conducting a survey of the levels and sources of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) and other dioxin-like substances into the environment (de Wit et al., 1989). Fish samples have been collected for analysis for a number of reasons including identifying "hot spots" and sources as well as studying biological differences based on species, age and geography. Muscle and liver samples taken from the same individuals have also been analyzed to determine if PCDD/F partition differently in these two tissues. PCDD/F results from 63 fish samples were analyzed using multivariate statistics.

MATERIALS AND METHODS

Muscle and liver samples were composites of several individuals except in two cases (see Table 1). Herring (*Clupea harengus*), whitefish (*Coregonus sp.*) and trout (*Salmo trutta*) from the Swedish coast of the Bothnian Sea were obtained from the National Food Administration. Pike (*Esox lucius*) from the Emån river were obtained from the Kalmar County Authorities. Pike from the Dala River and burbot (*Lota lota*) samples were obtained by the Environmental Protection Agency. Herring from the Karlskrona archipelago (Utklippan) of the Baltic Proper, Bothnian Sea and Swedish west coast, pike from Lakes Vanern, Vättern and Storvindeln and from Utklippan, cod (*Gaddus morhua*) from Utklippan, Arctic char (*Salvelinus alpinus*) from Lake Vättern and whitefish from Lake Storvindeln were obtained from the Swedish Museum of Natural History. Sample extraction, work-up and analysis using high resolution GC/MS were according to Bergqvist et al. All results are available on an on-line database (Strandell, 1990). Multivariate analysis was carried out using the SIRIUS program (Pattern Recognition Systems LTD, Norway). The data were transformed by taking the logarithms of the lipid weight values.

RESULTS AND DISCUSSION

The results of the PCDD/F analyses for fish samples not previously published are given in Table 1. Results from herring samples with SNV ID numbers 0001s001-010 can be found in Bergqvist et al.

Results from pike samples with SNV ID numbers 0002s003-011 can be found in Kjeller et al. (1990). Results for herring samples with SNV ID numbers 0001s015-017, whitefish with ID number 0008s004 and arctic char with ID number 0005s001 can be found in Asplund et al. (1990). Results for burbot liver samples with SNV ID numbers 0006s001-003 can be found in de Wit et al. (1990).

In order to determine if there are species differences in PCDD/F on a lipid weight basis, principal components analysis (PCA) was performed on pike, cod and herring taken at Utklippan in the Karlskrona archipelago (Baltic Proper). The analysis shows that although these three species have similar levels of PCDD/F on a lipid weight basis, the patterns are different although they come from the same area. These samples have different patterns for the lower chlorinated furans indicating possible differences in uptake and/or metabolism.

PCA of muscle and liver samples from two cod, three burbot and six pike composites shows that the paired muscle and liver samples from each composite lie quite near each other. The major clustering is species-based with the paired pike samples forming one cluster, the paired cod samples forming a second cluster and the paired burbot samples a third cluster. Using the scores from PCA, a correlation analysis can be made. This shows that both the levels and patterns of PCDD/F in muscle and in liver from the same individuals are correlated ($p < 0.01$) independent of species.

PCA was performed on all the fish muscle samples (n=52). The first principal component (PC) explains 40 % of the variance and represents the level of contamination. The second PC explains 15 % of the variance and represents differences in chlorination pattern. The data divide into at least two clusters, one containing the herring samples and the other containing all the pike, whitefish, trout, cod and Arctic char. The burbot are possibly a separate group. SIMCA analysis (Wold et al., 1977) shows that herring and pike make two separate classes that are significantly different from each other and all other fish muscle samples ($p < 0.05$). This indicates possible species specific uptake and metabolism of PCDD/F as well as differences in contamination levels because of different habitats. Herring are pelagic fish whereas pike are demersal.

PCA of the herring samples (n=18) results in three distinct clusters: Baltic herring caught in the fall, Baltic herring caught in the spring and Bothnian Sea herring caught in the spring. The first PC (contamination levels) explains 71 % of the variance and separates the fall from the spring Baltic herring. The second principal component (chlorination pattern) explains 10 % of the variance and separates the Baltic herring from the Bothnian Sea herring. The variables that are most important for this separation are 2,3,7,8-TeCDD and 2,3,7,8-TeCDF. This difference is probably explained by the presence of industries including pulp mills along the Swedish coast of the Bothnian Sea. SIMCA analysis shows that the three herring groups are significantly different from each other ($p < 0.05$). Only one herring sample was available from the Swedish west coast. This sample does not fall into any of the three classes.

PCA was performed on the pike muscle samples (n=23). The first PC explains 50 % of the variance (contamination levels) and the second PC explains 8 % of the variance (chlorination pattern). Samples from Lakes Vänern and Vättern build two overlapping groups that are not separable. The Lake Vättern samples cluster closer together, indicating a more homogeneous contamination, while the pike from Lake Vänern are more widely dispersed and show a definite contamination level trend. Specifically samples from the northern end of the lake are the most highly contaminated. The variables most important for this contamination are 2,3,7,8-TeCDD and 2,3,7,8-TeCDF. The reasons for this have been discussed in Kjeller et al. (1990). Paper bleaching plants are located at the northern ends of both lakes.

Generally, the differences seen in this PCA indicate that the main factor separating the other pike samples is differences in exposure. The pike from Lake Storvindeln and at the lower end of Emån river have very low PCDD/F levels and two pike samples from Utklippan also fall close to these two samples. These samples are separated from the main group along the first PC and thus represent background levels. The sample from Lake Järnsjön on Emån River separates from all other pike samples. Lake Järnsjön has been contaminated by large amounts of polychlorinated biphenyls released by a recycled paper plant. The sample from the lower end of the Dala River falls partway between the sample from Lake Järnsjön and the samples from Lakes Vänern and Vättern. This part of the Dala River has various kinds of industries.

Table 1. PCDD/F levels in fish muscle and liver samples in pg/g lipid. SNV ID nr is the Swedish Environmental Protection Agency sample identification number in the dioxin database. Fish in composite is the number of individuals in the sample. NTEQ is TCDD equivalents calculated according to the Nordic model (Ahlborg, 1989). < means not detected at this level. Paired muscle and liver samples taken from the same individuals are indicated by boxes.

Species	Herring	Herring	Herring	Herring	Herring	Pike	Pike	Pike	Pike	Pike	Pike	Pike
Tissue	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Liver	Muscle	Muscle	Liver
Water body	Bothnian Sea	Bothnian Sea	Bothnian Sea	Bothnian Sea	Baltic Sea	Emån River	Emån River	Lake Vattern	Lake Vattern	Lake Vattern	Lake Vattern	Lake Vattern
Place	Gävle	Soderhamn	Hudiks-vall	Sunds-vall	Utklip-pan	Jarnsjön	Kärrhul-tesjön	N. Vis-ingsö	N. Vis-ingso	Hus-kvarna	Hus-kvarna	Hus-kvarna
SNV ID nr	0001s011	0001s012	0001s013	0001s014	0001s018	0002s001	0002s002	0002s012	0002s028	0002s018	0002s019	0002s027
Lipid %	12.4	13.4	10.4	13.1	3.5	0.18	0.25	0.57	5.8	0.77	0.62	6.4
Fish in composite	15	15	15	15	20	1	1	3	3	5	5	5
Isomer												
2,3,7,8-TeCDD	20	20	18	18	26	33	12	65	55	29	55	58
1,2,3,7,8-PeCDD	27	31	26	26	69	17	12	47	57	48	79	94
1,2,3,4,7,8-HxCDD	2.5	2.8	3.0	2.9	8.0	<11	8.0	<5.3	<2.9	<1.3	<6.5	<1.1
1,2,3,6,7,8-HxCDD	26	28	25	24	40	<11	8.0	21	28	20	31	66
1,2,3,7,8,9-HxCDD	2.9	2.8	2.8	2.7	4.0	<11	<4	<5.3	<2.9	<1.3	<4.8	6.1
2,3,7,8-HpCDD	2.3	1.8	2.2	1.9	<0.9	<11	<4	<5.3	5.5	<1.3	<4.8	7.8
OCDD	3.1	1.8	1.0	1.0	2.6	33	20	8.8	5.9	7.8	9.7	6.7
2,3,7,8-TeCDF	97	105	106	84	83	330	180	330	340	230	480	530
1,2,3,7,8-PeCDF	32	32	33	31	74	28	12	32	41	36	60	69
2,3,4,7,8-PeCDF	170	194	154	153	370	100	32	110	152	129	242	297
1,2,3,4,7,8/9-HxCDF	11	10	11	9.2	31	11	4.0	7.0	9.7	6.5	13	17
1,2,3,6,7,8-HxCDF	12	12	11	11	34	5.6	<4	5.3	8.1	6.5	9.7	17
1,2,3,7,8,9-HxCDF	<0.1	0.3	<0.1	<0.1	<0.6	<11	<4	<3.5	<1.0	<1.3	<1.6	<0.3
2,3,4,6,7,8-HxCDF	8.1	9.7	8.0	7.3	27	<5.6	<4	<1.8	7.6	5.2	9.7	13
1,2,3,4,6,7,8-HpCDF	2.1	2.4	2.3	2.1	3.1	<5.5	<4	<3.5	1.7	<1.3	<1.6	3.0
1,2,3,4,7,8,9-HpCDF	<0.1	<0.1	<0.1	<0.1	<0.6	<11	<4	<5.3	<2.2	<1.3	<3.2	<0.5
OCDF	<0.2	<0.2	<0.2	<0.2	<0.9	<11	<8	<11	<3.6	<1.3	<6.5	<1.1
NTEQ	140	150	125	120	270	130	60	175	210	140	270	310

Table 1, continued.

Species	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Pike
Tissue	Muscle	Liver	Muscle	Muscle	Muscle	Liver	Muscle	Muscle	Liver	Liver	Muscle	Muscle
Water body	Lake Vattern	Lake Vättern	Lake Vattern	Lake Vänern	Lake Vänern	Lake Vänern	Lake Vänern	Lake Vanern	Lake Vanern	Lake Vanern	Lake Stor-vindeln	Baltic Sea
Place	N. of Hjo	N. of Hjo	N. of Hjo	Marie-stad	Marie-stad	Marie-stad	Dättern	Dättern	Katt-fjorden	Vass-botten		Utklip-pan
SNV ID nr	0002s020	0002s029	0002S021	0002s013	0002s017	0002s026	0002s022	0002s023	0002s024	0002s025	0002s014	0002s015
Lipid %	0.42	5.2	0.44	0.47	0.4	10.6	0.06	0.19	8.6	3 9	0.36	0.53
Fish in composite	5	5	5	5	5	5	5	5	5	5	4	5
Isomer												
2,3,7,8-TeCDD	50	33	55	170	190	150	67	21	870	31	<2.8	15
1,2,3,7,8-PeCDD	57	46	68	140	155	151	117	26	407	74	11	15
1,2,3,4,7,8-HxCDD	<4.8	<2.5	<6.8	<11	<2.5	6.9	<33	<11	<1.3	<2.1	<11	<7.5
1,2,3,6,7,8-HxCDD	24	25	18	62	63	87	<17	<5.3	279	33	<8.3	<5.7
1,2,3,7,8,9-HxCDD	<2.4	<2.7	<4.5	<11	10	10	<17	<11	24	3.3	<11	<7.5
2,3,7,8-HpCDD	<2.4	3.7	<4.5	<11	<2.5	10	<33	<16	22	14	<14	<9.4
OCDD	9.5	5.6	6.8	11	10	5.1	<33	<16	8.8	31	11	<11
2,3,7,8-TeCDF	381	327	409	617	725	651	650	216	3950	436	144	177
1,2,3,7,8-PeCDF	55	44	64	68	77	73	83	26	209	46	14	21
2,3,4,7,8-PeCDF	183	152	214	187	235	226	217	63	547	164	28	79
1,2,3,4,7,8/9-HxCDF	9.5	11	16	21	13	16	67	<5.3	76	13	5.6	5.7
1,2,3,6,7,8-HxCDF	9.5	7.7	9.1	15	15	20	17	<5.3	50	9.5	2.8	3.8
1,2,3,7,8,9-HxCDF	<2.4	<1.0	<2.3	<6.4	<2.5	<0.2	<17	<5.3	3.4	<0.5	<8.3	<5.7
2,3,4,6,7,8-HxCDF	7.1	6.3	6.8	<4.3	13	16	<17	<5.3	45	11	<5.6	<3.8
1,2,3,4,6,7,8-HpCDF	<2.4	2.1	<2.3	<6.4	<2.5	4.6	<17	<11	47.7	5.9	<8.3	<5.7
1,2,3,4,7,8,9-HpCDF	<2.4	<1.7	<2.3	<11	<2.5	<0.4	<33	<11	<0.6	<1	<14	<9.4
OCDF	<2.4	<2.9	<2.3	<19	<2.5	<0.8	<33	<16	9.8	<1.8	<25	<17
NTEQ	210	170	250	400	475	415	300	90	1740	200	40	80

Table 1, continued.

Species	Pike	Cod	Cod	Cod	Cod	Burbot	Burbot	Burbot	Trout	Whitefish	Whitefish	Whitefish
Tissue	Muscle	Muscle	Liver	Muscle	Liver	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle
Water body	Baltic Sea	Baltic Sea	Baltic Sea	Baltic Sea	Baltic Sea	Bothnian Bay	Torne River	Bothnian Bay	Bothnian Sea	Bothnian Sea	Bothnian Sea	Bothnian Sea
Place	Utklippan	Utklippan	Utklippan	Utklippan	Utklippan	Ltukrunni	Pajala	Seskaro	Sundsvall	Gavle	Soderhamn	Hudiksvall
SNV ID nr	0002s016	0003s001	0003s002	0003s003	0003s004	0006s004	0006s005	0006s006	0007s001	0008s001	0008s002	0008s003
Lipid %	0.47	0.77	70	0.51	67.1	0.76	0.51	0.69	5.6	5.2	4.1	4
Fish in composite	5	10	10	10	10	5	5	6		15	14	14
Isomer												
2,3,7,8-TeCDD	21	13	16	20	10	104	<3.9	58	25	54	44	35
1,2,3,7,8-PeCDD	26	5.2	8.4	9.8	6.1	65	<3.9	28	15	27	42	30
1,2,3,4,7,8-HxCDD	<8.5	<3.9	<1.0	<3.9	<0.3	<3.9	<5.9	<4.3	<0.2	<0.4	<0.2	<0.3
1,2,3,6,7,8-HxCDD	6.4	10	19	12	13	120	5.9	44	8.9	18	27	15
1,2,3,7,8,9-HxCDD	<8.5	<3.9	2.0	<3.9	1.8	6.6	<3.9	<4.3	<0.2	2.7	2.9	1.5
2,3,7,8-HpCDD	<8.5	<5.2	<1.2	<5.9	2.4	<2.6	<3.9	<4.3	<0.2	<0.2	<0.2	<0.3
OCDD	<13	3.9	1.9	12	0.8	28	9.8	10	1.3	2.3	2.2	2.0
2,3,7,8-TeCDF	180	77	94	98	70	340	37	230	93	330	290	325
1,2,3,7,8-PeCDF	30	29	36	39	27	15	3.9	12	12	25	27	33
2,3,4,7,8-PeCDF	130	44	57	53	42	67	9.8	51	114	117	150	150
1,2,3,4,7,8/9-HxCDF	8.5	9.1	12	12	8.2	2.6	5.9	2.9	1.6	3.8	5.1	5.3
1,2,3,6,7,8-HxCDF	6.4	13	17	14	10	1.3	2.0	1.4	2.5	3.1	4.1	4.8
1,2,3,7,8,9-HxCDF	<4.3	<2.6	<0.6	<3.9	<0.1	<2.6	<3.9	<2.9	<0.2	<0.2	<0.2	<0.3
2,3,4,6,7,8-HxCDF	<4.3	<2.6	14	7.8	8.6	<2.6	<3.9	<2.9	1.8	3.1	3.9	<3.8
1,2,3,4,6,7,8-HpCDF	<4.3	<2.6	<0.7	<3.9	1.8	<1.3	<2.0	<2.9	<0.2	1.3	1.5	1.5
1,2,3,4,7,8,9-HpCDF	<8.5	<5.2	<1.2	<5.9	<0.1	<2.6	<3.9	<4.3	<0.2	<0.2	<0.2	<0.3
OCDF	<17	<9.1	<2.3	<5.9	<0.2	<3.9	<5.9	<5.8	<0.2	<0.2	<0.2	<0.3
NTEQ	120	50	60	70	45	220	10	125	100	160	170	160

A number of fish samples are currently being analyzed. These represent several other species and geographical locations. The results from these samples will also be presented.

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