LEVELS OF NON-ORTHO POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED NAPHTHALENES IN FISH AND SEDIMENT SAMPLES

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ABSTRACT

Levels of pPCB and PCN were determined on a lipid weight basis in thirteen fish samples and on an ignition loss basis in eight sediment samples. Levels of PCN and pPCB were both low in fish and sediment from background areas. Fish from an industrialized coastline in Bothnian Bay also showed background levels although these have previously shown elevated PCDD/F levels. One fish sample from Lake Vänern had elevated PCN levels but low pPCB levels. Two fish from Lake Kyrksjön and two sediments from Lake Järnsjön showed both high PCN and high pPCB levels. These two lakes both have recycled paper plants upstream that are known to have released large amounts of PCB into the aquatic environment. Differences in PCN and pPCB levels can probably be attributed to different sources for these two groups of substances. No differences were seen in partitioning of PCN and pPCB in fish liver and muscle on a lipid weight basis.

INTRODUCTION

In addition to polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), the Swedish Dioxin Survey includes analyses of dioxin-like substances such as the non-ortho polychlorinated biphenyls (pPCB) 3,3',4',4'-tetrachlorinated biphenyl (IUPAC 77), 3,3',4,4',5-pentachlorinated biphenyl (IUPAC 126), 3,3',4,4',5,5'-hexachlorinated biphenyl (IUPAC 169) and polychlorinated naphthalenes (PCN). Previously we have analyzed a number of biological and sediment samples for pPCB and PCN (Asplund et al., 1990). In this study, additional sediment and fish samples were analyzed for pPCB and PCN to further investigate the concentrations and profiles of these substances and to try to identify sources. Muscle and liver samples from the same fish were also analyzed to compare partitioning in these tissues. These pPCB and PCN results are compared to PCDD/F results for the same samples (Kjeller et al., 1990; de Wit et al., 1990a; de Wit et al., 1990b) and also to previous pPCB and PCN results.

MATERIALS AND METHODS

Four sediment samples were collected at three sites on Emån river by the local authorities of Kalmar County: one surficial and one deep sediment sample (9-10 cm) from a PCB-contaminated lake (Lake Järnsjon), one surficial sediment sample taken upstream of Lake Järnsjön (Sjunnen) and one downstream of Lake Järnsjön (Grönskogssjön). Surficial sediment samples were collected by the Physical Geography Department, University of Umeå, at four sites along the Dala river from its origins in the mountains to near its mouth into the Baltic Sea. The lower end of this river is heavily industrialized. The fish samples were obtained via the Swedish Museum of Natural History, Swedish Environmental Protection Agency and Kalmar County authorities. Pike were collected from Lake Kyrksjön (PCB contaminated), Lake Storvindeln (background) and from the northern and southern end of the highly industrialized Lake Vänern. Burbot samples were collected from Torne river (Pajala-background) and from Etukrunni and Seskarö (near large industries), situated in Bothnian Bay. All samples were composites of 4-6 individuals except for the samples from Lake Kyrksjön. Sediment samples were extracted according to Jensen et al. (1977). Ignition loss was determined after heating to 550°C for 3 hours. The fish samples were homogenized and extracted and lipid weight was determined according to Jensen et al. (1983). After extraction the samples were cleaned-up, fractionated and analyzed according to Haglund et al. (1990), with some minor modifications. The method includes sulfuric acid/n-hexane partitioning, gel permeation chromatography, high performance liquid chromatography fractionation using a 2-

(1-pyrenyl)ethyldimethylsilylated silica column and analysis for pPCB and PCN using gas chromatography/mass spectrometry (GC/MS) according to Asplund et al. (1990). All results are available on an on-line database (Strandell, 1990).

RESULTS AND DISCUSSION

The results of the analyses are presented in Tables 1 and 2. The labelling of PCNs is according to their degree of chlorination (Te=tetra, Pe=penta, Hx=hexa, Hp=hepta) and elution order (a,b,c etc.) on a 5% phenyl methyl silicone GC column. The lowest levels of PCN and pPCB are seen in the pike from Lake Storvindeln and in all the burbot samples. Lake Storvindeln is a pristine mountain lake that is used as a background station within the Environmental Monitoring Programme. It probably receives contamination via the atmosphere. This same pike sample has been analyzed for PCDD/F and the levels were very low (de Wit et al., 1990b). Burbot samples from Pajala also come from a less disturbed area. The other two pairs of samples come from burbot collected in an area affected by industries (steel factory, pulp bleaching). There are no differences in the burbot samples based on collection site indicating that there is probably no large source of PCN or pPCB in this area. The burbot samples near the industrialized area do contain high levels of dioxins however (de Wit et al, 1990a), indicating that there is a source for these substances (Table 1). The major PCN congeners found in these samples are PeCN(a), PeCN(c) and HxCN(a) and IUPAC 77 is the major pPCB with levels twice those of IUPAC 126.

Pike samples from the southern (Vassbotten) and northern end (Kattfjorden) of Lake Vänern are very different from each other. PCN and pPCB levels in the Vassbotten samples are 4-5 times background levels while the samples from Kattfjorden have PCN levels 100 times background levels. The predominant congener is HxCN(a). Vassbotten and Kattfjorden have similar pPCB levels with IUPAC 77 levels equal to IUPAC 126 levels. The pike from Vänern have also been analyzed for PCDD/F (Kjeller et al., 1990). PCDD/F levels are very high in Kattfjorden (Table 1). There are several possible sources for PCN and PCDD/F at the northern end of the lake including a bleached pulp plant and a chemicals manufacturer.

Liver and muscle samples from the same individuals show very similar pPCB and PCN levels (lipid weight basis) in pike and burbot. This is in agreement with cod muscle and liver analyzed previously (Asplund et al, 1990). A similar relationship has been shown for PCDD/F (de Wit et al., 1990b).

The pike samples from Lake Kyrksjön have PCN levels 50-60 times background levels and pPCB levels 40-50 times background. The major PCN is PeCN(c) and IUPAC 77 dominates the pPCB with levels 10-15 times that of IUPAC 126. Previously, a pike sample from Lake Järnsjön on the Emån river was analyzed for PCN and pPCB (Asplund et al., 1990) and the levels are comparable to those from Lake Kyrksjön. The sediment samples from Emån river show low levels of both PCN and pPCB upstream of Lake Järnsjön, and very high levels of both groups at 0-1 cm and 9-10 cm in Lake Järnsjön. The pPCB levels are the same in both Järnsjön samples but the PCN levels are 4-5 times higher at 9-10 cm depth. This indicates a constant source of PCB over time but a different source of PCN that has been reduced over time. The sediment sample taken downstream has a similar pattern of PCN and pPCB as Lake Järnsjön but levels are ten times lower. The pike (de Wit et al., 1990b) and sediment samples (unpublished results) from Lake Järnsjön have been analyzed for PCDD/F. For pike the NTEQ is 55 pg/g lipid. NTEQ values for sediment samples are given in Table 2. The PCDD/F levels are fairly similar in all four sediment samples. Both Lake Järnsjön and Lake Kyrksjön are contaminated by PCBs from nearby recycled paper plants.

Sediment samples from three sites on the Dala river contain no PCN and very little pPCB. However, the sample from Hedesundafjärden does contain PCN. The stretch of the river from Hovran to Hedesundafjärden has numerous industries which could be sources of PCN. The PCDD/F levels in these samples follows a similar pattern with low levels in the three upstream sites and higher levels at Hedesundafjärden (Kjeller et al, 1990).

These results indicate that there are different sources for PCN, pPCB and PCDD/F and that low levels of one group of contaminants do not necessarily mean that the others are not present. This can create problems when calculating the toxic potential of contaminants in samples. Fig. 1 illustrates this. For some biological samples, PCDD/F are major contributors to the toxic potential expressed as TCDD equivalents. But for the majority, pPCB contributes more. The toxic potential of PCN is still

Table 1. PCN and pPCB in fish samples given in ng/g lipid weight. SNV ID nr is the Swedish Environmental Protection Agency sample identification number in the dioxin database. n is number of fish in composite. The labelling of PCNs is according to their degree of chlorination (Te=tetra, Pe=penta, Hx=hexa, Hp=hepta) and elution order (a,b,c etc). < or nd means not detected a this level. (1)-peak area has been integrated together with TeCN(f) due to insufficient chromatographic separation. NA means not analyzed. PCDD/F NTEQ is TCDD equivalents calculated according to the Nordic model (Ahlborg, 1989). NTEQ values are given in pg/ lipid and are taken from Kjeller et al., 1990; de Wit et al, 1990a; 1990b. Paired muscle and liver samples taken from the same individuals are indicated by boxes.

Species	Pike	Pike	Pike	Pike	Pike	Pike	Pike	Burbot	Burbot	Burbot	Burbot	Burbot	Burbot
Tissue	muscle	muscle	liver	muscle	liver	muscle	muscle	liver	muscle	liver	muscle	liver	muscle
Water body	Lake Stor-	Lake Vänern	Lake Vänern	Lake Vänern	Lake Vänern	Lake Kyrksjon	Lake Kyrksjon	Bothnian Bay	Bothnian Bay	Torne River	Torne River	Bothnian Bay	Bothnian Bay
Place	vindeln	Katt-fjorden	Katt-fjorden	Vass-botten	Vass-botten			Etuk-runni	Etuk-runni	Pajala	Pajala	Seskaro	Seskaro
SNV ID nr	0002s014	0002s004	0002s024	0002s006	0002s025	Pike 01	Pike 02	0006s001	0006s004	0006s002	0006s005	0006s003	0006s006
Lipid %	0.58	0.53	8.97	0.48	4.45	0.65	0.68	48.6	0.63	21.2	0.49	51.5	0.71
n	4	5	5	5	5	1	1	5	5	5	5	6	6
TeCN(a)	0.15	2.1	4.8	0.62	1.3	7.5	5.4	0.11	0.21	0.14	0.19	0.06	0.21
TeCN(b)	0.17	0.84	1.9	0.51	1.2	3.0	2.8	0.08	0.21	0.15	0.21	0.05	0.21
TeCN(c)	0.13	0.45	1.3	0.36	nd	2.4	2.1	0.05	0.15	0.12	0.15	0.03	0.11
TeCN(d)	0.13	0.37	1.1	0.31	nd	2.0	1.9	0.06	0.18	0.11	0.15	0.04	0.14
TeCN(e)	nd(1)	0.28	nd	nd(1)	nd	nd	0.27	0.04	nd	nd	nd	nd	0.08
TeCN(f)	0.11	0.30	nd	0.29	nd	0.80	0.61	0.07	0.19	0.11	0.15	0.04	0.14
TeCN(g)	0.14	0.30	nd	0.31	nd	0.51	0.43	0.04	0.17	0.10	0.16	0.03	0.13
Total TeCN	0.83	4.7	9.0	2.4	2.4	16	14	0.46	1.1	0.72	1.0	0.24	1.0
PeCN(a)	0.49	29	43	3.5	4.8	42	30	0.37	0.78	0.36	0.45	0.18	0.78
PeCN(b)	nd	6.3	8.7	0.72	0.97	6.1	4.5	0.09	0.21	nd	nd	0.04	0.18
PeCN(c)	0.22	3.9	6.2	1.8	2.6	49	32	0.22	0.63	0.25	0.36	0.11	0.58
PeCN(d)	0.10	2.5	3.4	0.42	nd	3.7	3.2	nd	nd	0.09	0.12	0.03	0.12
PeCN(e)	0.13	0.55	1.2	0.38	nd	6.3	5.0	0.06	0.18	0.10	0.14	0.03	0.13
PeCN(f)	0.11	1.3	2.2	0.70	1.0	14	11	0.07	0.20	0.12	0.18	0.03	0.14
PeCN(g)	0.10	1.2	2.2	0.54	nd	9.3	8.1	0.07	0.23	0.11	0.15	0.03	0.15
PeCN(h)	0.12	1.1	2.1	0.60	1.0	13	11	0.08	0.34	0.11	0.19	0.05	0.22
Total PeCN	1.3	46	69	8.6	11	140	100	0.96	2.6	1.1	1.6	0.50	2.3
HxCN(a)	0.39	87	120	2.6	2.8	2.4	1.8	0.28	0.61	0.13	0.21	0.11	0.56
HxCN(b)	0.02	29	35	0.38	0.33	2.5	1.6	0.10	0.11	<0.02	<0.06	0.03	0.11
HxCN(c)	<0.02	19	23	0.38	nd	4.6	3.0	0.19	0.27	<0.02	<0.06	0.05	0.23
HxCN(d)	0.05	7.8	8.6	0.53	0.58	4.7	3.5	0.06	0.26	0.03	0.08	0.05	0.14
HxCN(e)	nd	5.2	5.8	<0.05	nd	0.43	0.35	nd	nd	nd	nd	<0.01	nd
Total HxCN	0.46	150	190	3.9	3.7	15	10	0.62	1.3	0.16	0.29	0.24	1.04
HpCN(a)	<0.1	8.6	16	nd	nd	0.05	0.09	<0.04	<0.3	nd	<0.3	<0.03	0.04
HpCN(b)	nd	3.1	3.9	nd	nd	nd	<0.04	nd	nd	nd	nd	nd	nd
Total PCN	2.6	210	290	15	17	170	130	2.0	4.9	2.0	2.9	0.98	4.4
IUPAC 77	1.1	6.7	16	4.2	8.5	77	55	0.43	1.0	0.89	0.88	0.28	0.96
IUPAC 126	0.64	6.7	17	5.5	8.2	6.5	3.1	0.33	0.59	0.69	0.54	0.19	0.52
IUPAC 169	0.22	0.34	1.1	0.29	0.30	0.42	<0.15	<0.02	<0.04	<0.08	<0.04	<0.01	<0.02
Total pPCB	2.0	14	34	10	17	84	58	0.76	1.6	1.6	1.4	0.47	1.5
PCDD/F NTEQ	40	1400	1700	290	200	NA	NA	290	220	4	10	170	125

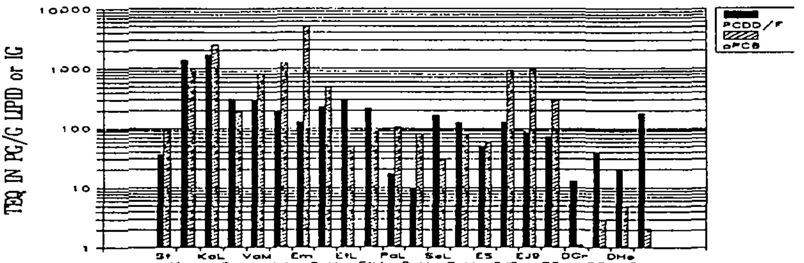

Fig. 1. Comparison of TCDD equivalents (TEQ) for pPCB and PCDD/F in fish and sediment. For PCDD/F the Nordic model is used. Toxic equivalency factors for pPCB are averages of AHH and EROD enzyme induction reported by Hanberg et al. (1990). These are 0.001 for IUPAC 77, 0.15 for IUPAC 126 and 0.006 for IUPAC 169. Pike are from Storvindeln (St), Kattfjorden (Ka), Sandviken (Sa), Vassbotten (Va) and Järnsjön (Em). Herring are from the Baltic (BaH), burbot from Etukrunni (Et), Pajala (Pa) and Seskarö (Se). Sediment is from Emån river at Sjunnen (ES), Jarnsjön 0-1 cm (EJ0), Järnsjön 9-10 cm (EJ9), Grönskogsjön (EG) and the Dala river at Grövelsjön (DGr), Siljan (DSi), Hovran (DHo) and Hedesundafjärden (DHe).

Table 2. PCN and pPCN in sediment samples given in ng/g ignition loss (IG %). SNV ID nr is the Swedish Environmental Protection Agency sample identification number in the dioxin database. nd means not detected. (1) means not integrated. For explanation of PCN labelling see legend to Fig. 1. PCDD/F NTEQ is TCDD equivalents calculated according to the Nordic model. NTEQ values are given in pg/g IG % and values are taken from Kjeller et al., 1990 for Dala river. For Emån river, unpublished results.

River	Emån	Emån	Emån	Emån	Dala	Dala	Dala	Dala
Place	Sjunnen	Jarnsjön 0-1 cm	Järnsjön 9-10 cm	Grön-skogssjön	Grovel-sjön	Siljan	Hovran	Hedesunda-fjärden
SNV ID nr	0310s004	0310s002	0310s003	0310s001	0320s001	0320s002	0320s003	0320s004
IG %	65	17	27	15	21	7	6	12
TeCN(b)	0.34	28	100	3.3	nd	nd	nd	1.0
TeCN(c)	0.28	14	67	2.2	nd	nd	nd	0.92
TeCN(d)	0.28	21	63	2.3	nd	nd	nd	1.0
TeCN(e)	nd	3.3	13	nd	nd	nd	nd	nd
TeCN(f)	0.26	11	19	1.5	nd	nd	nd	nd
TeCN(g)	0.38	41	190	4.9	nd	nd	nd	1.2
Total TeCN	1.5	118	450	14	nd	nd	nd	4.1
PeCN(a)	0.34	12	72	3.3	nd	nd	nd	5.7
PeCN(b)	nd	2.2	nd(1)	nd	nd	nd	nd	1.6
PeCN(c)	0.31	21	130	4.2	nd	nd	nd	0.92
PeCN(d)	nd	6.7	38	1.9	nd	nd	nd	1.3
PeCN(e)	0.28	13	82	2.9	nd	nd	nd	1.1
PeCN(f)	0.32	17	100	3.5	nd	nd	nd	1.2
PeCN(g)	0.31	16	88	3.4	nd	nd	nd	1.3
PeCN(h)	0.37	28	140	3.9	nd	nd	nd	1.5
Total PeCN	1.6	85	510	23	nd	nd	nd	13
HxCN(a)	nd	1.9	2.9	2.1	nd	nd	nd	1.9
HxCN(b)	nd	2.1	3.7	nd	nd	nd	nd	1.9
HxCN(c)	nd	2.5	5.5	2.1	nd	nd	nd	2.0
HxCN(d)	nd	1.9	5.2	0.93	nd	nd	nd	1.1
HxCN(e)	nd	0.65	2.4	nd	nd	nd	nd	1.8
Total HxCN	nd	9.1	20	5.2	nd	nd	nd	8.7
Total PCN	3.1	210	980	42	nd	nd	nd	26
IUPAC 77	0.83	420	420	43	1.0	2.9	4.8	2.1
IUPAC 126	0.37	3.4	3.5	1.7	nd	nd	nd	nd
IUPAC 169	0.02	0.06	nd	nd	nd	nd	nd	nd
Total pPCB	1.2	425	425	45	1.0	2.9	4.8	2.1
PCDD/F NTEQ	48	130	85	73	13	37	19	180

being determined. Therefore it is very important to include not only PCDD/F analyses but also analyses of dioxin-like substances such as PCN and pPCB.

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