Characterization and fate of polychlorinated biphenyl contaminants in Kernaalanjärvi sediments

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Polychlorinated biphenyl (PCB) content and distribution of individual PCB congeners in sediment samples from Kernaalanjärvi, a lake in Finland, were determined with a gas chromatography-electron/capture detection (GC-ECD) technique. Three different extraction methods with hexane–acetone mixture were tested. Neither extended extraction time (1 day vs. 10 days) nor sonication increased the recovery of PCBs from the aged sediments. For freshly spiked PCBs the extraction efficiency was $93\% \pm 2\%$ (w/w). Total PCB concentrations ranging from 0.5 to 10.7 mg kg⁻¹ d.w. were measured in Kernaalanjärvi sediment samples from the 2–15 cm depth. Comparison of PCB discharge documentation to congener distribution patterns in sediments suggested selective removal of lower chlorinated PCBs by physical processes. There was no evidence of *in situ* biotransformations of PCBs by indigenous sediment microorganisms. Presence of potentially toxic mono- and di-*ortho* chlorinated coplanar PCBs in sediments resulted in estimated 2,3,7,8-TCDD (tetrachlorodibenzo-*p*-dioxin) toxic equivalents between 15 and 301 ng kg⁻¹ d.w.

Introduction

Freshwater and marine sediments serve as sinks for many synthetic chemicals. Some contaminants are recalcitrant in sediments whereas others shift between different physical compartments or are transformed in various ways (Calmano *et al.* 1996). Contaminating substances are frequently technical mixtures of different homologs and isomers from the same chemical group (e.g. polychlorinated biphenyls, polyaromatic hydrocarbons). Each component in a mixture may move and be transformed at different rates, which results in changes in pollutant mixture profiles in a given sediment location over time.

Polychlorinated biphenyls (PCBs) are among more common organochlorine compounds that typically accumulate in sediments. PCBs were used as complex mixtures of individual congeners in various applications including heat transfer, dielec-



tric, and hydraulic fluids, flame retardants, and plasticizers (Abramowicz 1990). PCBs were never introduced to nature by design as was the case with pesticides. Nevertheless, the environmental PCB load is estimated to exceed 350 000 tonnes which corresponds to one third of the total world production (Tanabe 1988).

PCBs are characterized by excellent oxidative and thermal stability, and were long believed to be recalcitrant in the environment. However, it has now been shown that both aerobic and anaerobic microorganisms can transform PCBs (for reviews, *see* e.g. Abramowicz 1990, Unterman 1996). Furthermore, there are several reports confirming *in situ* biotransformations of PCBs both in the presence and absence of oxygen (Brown *et al.* 1987, Brown and Wagner 1990, Flanagan and May 1993, Bedard and May 1996).

Physical phenomena such as sorption, desorption, dissolution, and volatilization affect PCB concentrations and distribution in contaminated sediments. The composition of the PCB mixture and the characteristics of the contaminated site determine the importance of these processes. For example, Kannan *et al.* (1997) reported extensive contamination of soil and marsh sediments with highly chlorinated Aroclor 1268. The PCB congener profile in sediment samples corresponded to Aroclor 1268 suggesting high stability of this PCB mixture. PCBs were strongly bound by the sediment environment; over a 50-fold decline in total PCBs with a distance of 500 meters away from the discharge point was reported.

Our goal was to characterize the PCB contamination of Kernaalanjärvi, a lake in Finland, using selected sediment samples, and to determine whether or not the composition of the original PCB mixture in the sediments has changed as a result of biological or other processes. Although the PCB content in Kernaalanjärvi sediments was previously studied, the distribution of individual PCB congeners is not reported (Kansanen and Pilke 1987, Kansanen et al. 1990, Kansanen et al. 1991). Previous observations concerning in situ biotransformations of PCBs were from sites under moderately temperate climate, i.e. between 40° and 50° northern latitude (Brown et al. 1987, Brown and Wagner 1990, Flanagan and May 1993, Bedard and May 1996). It was in our interest to study whether or not these in situ biotransformations occurred under boreal conditions (60-65° northern latitude), where water temperature approaches 4 °C.

Materials and methods

Site description and sample collection

Kernaalanjärvi is a lake located in southern Finland, in the municipality of Janakkala (Fig. 1). The surface area of the lake is 4.7 km² with a mean depth of 4 m. In 1956–1984, approximately 9001 (1 250 kg) of PCB oils were discharged into the lake from the research laboratory of a paper mill manufacturing dielectric paper (Waltari et al. 1987). The exact composition of the PCB load is not known, but it consisted of Clophen A50 mixture with pentachlorobiphenyls as the main PCB congeners and of several Pyralene and Aroclor mixtures with mostly tri- and tetrachlorinated PCB components. Use of Clophen A50 in test capacitors ceased in the 1960s when it was replaced by the lower chlorinated PCB mixtures. It has been estimated that 100 l of Clophen A50 and 800 l of the other PCB mixtures were discharged to Kernaalanjärvi (Waltari et al. 1987). Therefore, the main sediment contaminants were originally tri- and tetrachlorobiphenyls. Previous gas chromatographic



(GC) analyses, performed by comparison of sediment PCB profiles to standard chromatograms with known Aroclor compositions and contents, suggested that the total concentrations of extractable PCBs in Kernaalanjärvi sediments did not exceed 15 mg kg⁻¹ d.w. (Kansanen *et al.* 1990). The concentrations of individual PCB congeners have not been previously reported.

Sediment samples were collected from three locations in Kernaalanjärvi (Fig. 1). Sampling site A was situated in the most contaminated region near the mouth of the Tervajoki, which is the original source of PCBs to the lake (Kansanen and Pilke 1987). Other main inflows to the lake have been shown to be noncontaminated with PCBs; thus reference site C was expected to contain relatively low PCB levels. The water depth at locations A and C was 2 m. The third sampling point (site B) was in the accumulation zone with a water depth of 8 m. The sedimentation rate in this accumulation zone is approximately 0.2 g cm⁻² a⁻¹ when neglecting the influence of resuspension (Kansanen *et al.* 1991).

Samples were taken in October 1995 when the water temperature was 10 °C. A plexiglass sampling tube (i.d. 45 mm) was used to collect approximately 15-cm sediment cores from the lake bottom. Three to five samples were taken from each sampling point to compose two separate combination samples. A 2-cm proportion from the top of each profile was separated for the enrichment of aerobic PCB degrading cultures (Hurme and Puhakka 1997). The remaining subsurface sediment (2-15 cm) from three parallel samples was combined to achieve a total sample volume of 0.6 l. This proportion was used in anaerobic degradation experiments (Hurme and Puhakka 1997) and for PCB quantification. Samples were collected in glass jars that were filled with the lake water and stored at 8 °C.

Sediment analyses

Sediment samples were analyzed for their organic carbon and PCB content. Organic carbon was measured according to the standard method SFS 3008 (Finnish Standards Association 1990) as a difference of total solids and total fixed residue. The organic carbon content in the three sediment samples ranged from 11% to 14%.

Extraction of PCBs from the sediment was conducted in 15-ml test tubes sealed with teflon lined rubber septa and screw-caps. Sediment samples were thoroughly mixed with the lake water and 10.0 or 12.5-ml subsamples were transferred into triplicate tubes. The amount of dry sediment in each tube was approximately 2 g. With the site A sediment, three different extraction techniques were tested and nine parallel tubes were used. After centrifuging (3 000 rpm, 3 min) the supernatant was discarded and octachloronaphthalene (OCN, 2.48 nmol) was added as an internal standard. In preliminary experiments using site A sediment, the supernatant was extracted with 2 ml of hexane and analyzed. No observable amounts of PCBs were found in the extract.

Sediment samples were extracted twice with 6 ml of hexane–acetone (1:1) mixture. In the first stage, triplicate samples from three sampling sites were set on a shaker for 16–20 h (method 1), whereas the additional samples of site A sediment were either shaken for 10 days (method 2) or sonicated for 5 min (method 3). In the second stage, all samples were shaken with solvent mixture for 5 min, and the solvent phases from the two steps were combined in a separatory funnel. Solids remaining after the extraction were dried at 105 °C, and the dry weight was measured for the normalization of PCB concentrations.

Acetone was removed from the extracts by reverse partitioning into distilled water $(2 \times 10 \text{ ml})$ in a separatory funnel. The remaining hexane fractions were concentrated to less than 2 ml under a nitrogen stream, and passed through a Florisil column (0.5 g in a Pasteur pipette). PCBs were eluted from the column into a weighed glass vial with 4 ml of hexane. The sample was further concentrated to approximately 1 ml, and the vial was weighed to determine the exact hexane volume. Elemental sulfur, which interferes during GC analysis, was removed with a reagent prepared by adding 3.39 g of tetrabutylammonium (TBA) hydrogen sulfate in 100 ml of distilled water and by saturating the solution with 25 g of sodium sulfite (Jensen et al. 1977). This TBA sulfite reagent (1 ml) was vigorously shaken with the extract, and the upper hexane fraction was collected for GC analysis.

PCB extraction efficiency from freshly spiked

sediment was determined with method 1 alone. The PCB addition was 40 µg of either Aroclor 1242 or Aroclor 1254 to approximately 2 g (d.w.) of site C sediment. In these tests, PCBs were analyzed also from the supernatant. The PCB recovery (\pm SD) achieved for six samples was 93% $\pm 2\%$ (w/w). As compared to the sediment samples with aged PCBs, there was a significant proportion $(30\% \pm 4\%)$ of PCBs present in the supernatant, and $63\% \pm 4\%$ was recovered from the sediment. Proportions of individual congeners remained relatively unchanged in both extracts as compared to the original PCB mixtures. Most variation was observed in the sediment extracts of Aroclor 1242 spiked samples, where the relative proportions of penta- and hexa-CBs increased by 4.7%-4.9%, and the proportions of di-, tri-, and tetra-CBs decreased by 2.3%-4.6%. The extraction efficiency value was not used to correct the PCB results of Kernaalanjärvi sediments.

Congener-specific PCB analysis

PCBs were analyzed with a Hewlett-Packard 5890 Series II GC equipped with a HP-5 fused-silica column (length 25 m, i.d. 0.32 mm, film thickness 0.52 μ m), a ⁶³Ni electron capture detector, and a HP 7673 automatic liquid sampler. Helium served as the carrier gas (5 ml min⁻¹) and argonmethane mixture (19:1) as the makeup gas (50 ml min⁻¹). The injector and detector temperatures were 250 °C and 320 °C, respectively. The initial oven temperature was 60 °C, from which it was ramped at 20 °C min⁻¹ to 160 °C, 3 °C min⁻¹ to 250 °C, and 10 °C min⁻¹ to 270 °C, and finally held for 5 min.

Aroclor 1242 and Aroclor 1254 mixtures used separately served as standards for identification of PCB congeners. These commercial PCB mixtures were used by us as estimates of the contaminants discharged to Kernaalanjärvi. GC profiles of the two Aroclors were matched with the chromatograms published by Schulz *et al.* (1989), Bedard *et al.* (1987), and Ivanov and Sandell (1992). Single congeners 25-25-CB, 245-25-CB, and 245-245-CB were also used for the identification. Relative retention times of all peaks in relation to OCN were calculated and compared to those reported by Mullin *et al.* (1984). The PCB congener names and IUPAC numbers assigned for the GC peaks in this study are given in Table 1.

Sediment PCBs were quantified with four point calibration curves of both Aroclor 1242 and 1254 as described by Eisenreich (1987). The concentrations of individual congeners in standard samples were calculated from the total PCB content and the weight percent distribution of congeners in the Aroclor mixtures according to Schulz *et al.* (1989). The relation between the response area and concentration was determined, and for each chromatographic peak an individual linear estimation line was calculated. The total sediment PCB content was the sum of the concentrations assigned for single peaks.

Results and discussion

Extraction techniques

Desorption of PCBs from the site A sediment was studied with three different extraction techniques. In addition to simply shaking the sample overnight with hexane/acetone mixture (method 1), an extended extraction period of 10 days (method 2) or extraction in a sonicator for 5 min (method 3) were tested. Longer extraction time was expected to enhance the recovery of PCBs, since sorbed organic compounds often display biphasic desorption kinetics i.e. a labile portion is released more readily as compared to the resistant, slowly desorbing component (Pignatello and Xing 1996). Sonication, on the other hand, could improve extraction by dissociating the complex sediment matrix.

The total PCB yields of 10.7 ± 0.6 , 9.2 ± 1.2 , and 8.9 ± 0.5 mg kg⁻¹ d.w. were achieved for triplicate site A samples extracted with methods 1, 2, and 3, respectively. In this study, neither longer extraction time nor the use of sonication enhanced the PCB recovery from aged sediment samples. Method 1 was most efficient for all PCB homologs from di- to octachlorinated congeners, and it was selected for further sediment characterization.

Quantification of sediment PCBs

Congener-specific PCB analysis was performed on the sediment samples from three different sampling locations of Kernaalanjärvi. The total PCB concentrations detected in triplicate samples from sites A, B, and C were 10.7 ± 0.6 , 1.2 ± 0.1 , and 0.53 ± 0.01 mg kg⁻¹ d.w., respectively. These results, representing average PCB concentrations in the sediment depth of 2–15 cm, correspond with previous measurements of surface sediment PCB levels in different parts of Kernaalanjärvi (Fig. 2) (Kansanen *et al.* 1990).

Fig. 3 shows PCB congener distributions measured in the three sediment samples and, for comparison, the corresponding profiles for Aroclors 1242 and 1254. Aroclor mixtures do not represent the original PCB load, but are indicative of the type of PCB contamination. Considering the discharge history, the similarity of the site A profile with that of Aroclor 1254 was surprising. Homolog distribution of extractable PCB congeners in sediment samples, and in Aroclor 1242 and 1254 mixtures are presented in Fig. 4. Pentachlorinated PCBs were most abundant in all the sediment samples as well as in Aroclor 1254. Since tri- and tetrachlorinated PCBs were originally the main contaminant groups, then significant removal of

Table 1. PCB congener assignment for gas chromatographic peaks. The major constituents of peaks consisting of two congeners are indicated with bold IUPAC numbers and substitution patterns.

Peak	IUPAC no.	Chlorine substitution	Peak	IUPAC no.	Chlorine substitution
1	10 + 4	26 + 2-2	37	119	246-34
2	7 + 9	24 + 25	38	83	235-23
3	6	2-3	39	97	245-23
4	8 + 5	2-4 + 23	40	115 + 87	2346-4 + 234-25
5	19	26-2	41	85	234-24
6	18	25-2	42	136	236-236
7	15 + 17	4-4 + 24-2	43	77 + 110	34-34 + 236-34
8	24 + 27	236 + 26-3	44	82 + 151	234-23 + 2356-25
9	16 + 32	23-2 + 26-4	45	135	235-236
10	29	245	46	109	235-34
11	26	25-3	47	123 + 149	345-24 + 236-245
12	25	24-3	48	118	245-34
13	31	25-4	49	134	2356-23
14	28	24-4	50	131	2346-23
15	33 + 53	34-2 + 25-26	51	122	345-23
16	51	24-26	52	146	235-245
17	22	23-4	53	153	245-245
18	45	236-2	54	132 + 105	234-236 + 234-34
19	46	23-26	55	141 + 179	2345-25 + 2356-236
20	52	25-25	56	130	234-235
21	49	24-25	57	176 + 137	2346-236 + 2345-24
22	47 + 48	24-24 + 245-2	58	138	234-245
23	44	23-25	59	158	2346-34
24	59 + 42	236-3 + 23-24	60	129 + 178	2345-23 + 2356-235
25	41 + 64	234-2 + 236-4	61	175	2346-235
26	40	23-23	62	187	2356-245
27	100 + 67	246-24 + 245-3	63	183	2346-245
28	63	235-4	64	128	234-234
29	74	245-4	65	167	245-345
30	70	25-34	66	174	2345-236
31	66 + 95	24-34 + 236-25	67	177	2356-234
32	91	236-24	68	171 + 156	2346-234 + 2345-34
33	56 + 60	23-34 + 234-4	69	173 + 201	23456-23 + 2346-2356
34	92 + 84	235-25 + 236-23	70	172	2345-235
35	90 + 101	235-24 + 245-25	71	180	2345-245
36	99	245-24	72	170 + 190	2345-234 + 23456-34

Fig. 2. Average PCB concentrations (mg kg⁻¹ d.w.) in the surface sediment samples (0–2 cm) of Kernaalanjärvi as reported by Kansanen *et al.* (1990).

lower chlorinated PCBs has occurred from the sediments.

Fate of PCBs in Kernaalanjärvi

Several physical and biological processes may be responsible for the PCB patterns observed in Kernaalanjärvi sediment samples. Chemical transformations are unlikely for inert PCBs. The preferential loss of lower chlorinated congeners has likely resulted from congener-selective processes such as dissolution, volatilization, and biotransformation. To understand the fate of PCBs in Kernaalanjärvi, the PCB loads in different physical compartments of the lake were reviewed together with principal processes affecting PCBs.

Sediment

Kansanen *et al.* (1990) reported that the total amount of PCBs in Kernaalanjärvi sediment is 1 100–1 200 kg, which corresponds the overall discharge to the lake. This estimate was based on 34 surface sediment samples (0–2 cm) and three sediment profiles (0–30 cm) that were analyzed in 2-cm segments. PCB quantification was conducted by comparison of the total response areas in sediment samples and in certain Aroclor mixtures. Characterization of the PCB mixture composition in sediment samples was ignored. Although their calculations suggested high persistence of PCBs in Kernaalanjärvi, they also estimated that 100–200 kg of PCBs could be found in sediments downstream the lake. A higher number of sediment profiles is needed to accurately determine the total sediment PCB content in Kernaalanjärvi. In the absence of such information, we can only examine other possible fates of PCBs.

Water mass

PCBs may exist in the water mass in two forms: dissolved or adsorbed onto particles. The dissolved phase contains colloidal matter (e.g. humus) that binds PCBs (Eisenreich 1987, Kukkonen and Oikari 1991). The water solubility of PCBs inversely correlates with the chlorine content; therefore, dissolution may have resulted in selective removal of lower chlorinated PCBs from the sediment. With suspended solids concentrations less than 10 mg l⁻¹, the fraction of dissolved PCBs is typically higher than the amount of PCBs in the particulate phase (Eisenreich 1987). In Kernaalanjärvi, the suspended solids concentration is near 10 mg l⁻¹, and the particulate phase PCB concentrations range from 0.01 to 0.07 µg l⁻¹ depending on the sampling site and the time of year (Kansanen et al. 1990, 1991). The average PCB concentration in the water phase of Kernaalanjärvi including both dissolved and particulate bound PCBs is thus roughly estimated to be at least $0.04 \,\mu g$ 1⁻¹. On that basis, there may be about 1 kg of PCBs presently associated with the water.

From the water phase PCBs may accumulate within living organisms or sorb back onto sediments at a less contaminated location. Moreover, run-off or volatilization may result in complete removal of water-bound PCBs from the lake. The outflow from Kernaalanjärvi is through Hiidenjoki, which during the years 1981–1990 had a mean discharge of 18.9 m s⁻¹ (Hydrological Yearbook 1990, KVVY 1997). Kernaalanjärvi delivers two thirds of this water and the rest comes from the Puujoki (KVVY 1997). With the estimated PCB concentration of 0.04 μ g l⁻¹ in the Kernaalanjärvi





Fig. 3. Distribution of PCB congeners in Kernaalanjärvi sediment samples (2–15 cm) and in Aroclor 1242 and 1254 mixtures.

water mass, an annual PCB discharge of 16 kg from the lake is expected. Most of the PCBs were discharged to Kernaalanjärvi before 1970. If the prevailing conditions have been stable during the last 30 years, 480 kg of PCBs may have escaped the lake. This is considerably more than the estimate made by Kansanen *et al.* (1990), which was based on the PCB concentrations in three surface sediment samples downstream of Kernaalanjärvi.

Considering the initial 900-liter (1 250 kg) discharge of the PCB mixtures to the lake, the proposed run-off corresponds to over one third of this iment samples (2-15 cm) and in Aroclor 1242 and 1254 load. If a mixture of Aroclor 1242 and Aroclor

1254 (88:12 w/w) is regarded as an estimate of the original load, then the share of di- and trichlorobiphenyls would have initially been 535 kg. Dissolution followed by run-off could thus well explain the loss of lower chlorinated PCBs from the sediment.

Water-air interface

Henry's law constants for PCBs are independent of the degree of chlorine substitution (Burkhard et al. 1985). Therefore, individual PCB congeners are volatilized from solid state at approximately equal rates. In watercourses, however, volatilization of PCBs occurs from the dissolved state in the air-water interface, and is thus proportional to the solubility of congeners. Achman et al. (1993) studied volatilization of PCBs in natural aquatic conditions from Lake Michigan, where water column PCB concentrations are lower than in Kernaalanjärvi. Net volatilization rates between 10 and 1 000 ng m⁻² d⁻¹ were measured. In the case of Kernaalanjärvi this would result in an annual PCB loss of 0.02-1.7 kg. During a 30-year period, 1-50 kg of PCBs may have volatilized from the lake, which is minor as compared to the outflow. Main factors influencing the extent of PCB volatilization in the air-water interface are dissolved PCB concentrations, wind speed, and temperature (Achman et al. 1993).

Bioaccumulation

Aquatic organisms take up PCBs through ingestion and direct partitioning from water into lipids (Shaw 1993). Octanol-water partition coefficients (K_{ow}) describe the bioaccumulation potential of hydrophobic compounds. Lipophilicity increases with increasing degree of chlorine substitution, and coplanar PCBs and their mono- and di-ortho substituted congeners exhibit higher lipophilicity as compared to non-coplanar PCBs. These compounds possessing two para chlorines and at least one meta chlorine, are detected in significant levels in environmental samples although their proportion in PCB products is typically low (Shaw 1993). In this study, di-ortho coplanar PCBs assigned to peaks no. 53 (245-245-CB) and 58 (234-245) were present in relatively high proportions at sites B and C. Bioaccumulation of coplanar PCBs in fish tissue followed by death of the organisms may have resulted in these patterns. Total PCB concentrations in perch, bream, and pike in Kernaalanjärvi have been reported to be close to 1 mg kg⁻¹ fresh weight (Kansanen et al. 1990). The distribution of individual PCB congeners in fish has not been reported.

Aerobic degradation

Verification of aerobic PCB biodegradation in sediments requires the detection of degradation products such as chlorobenzoic acids as reported by Flanagan and May (1993). In the absence of such evidence, it can be presumed that aerobic microbial degradation may have partially resulted in the loss of lower chlorinated PCBs from the sediments. In aqueous phase experiments with aerobic biphenyl degrading enrichment from Kernaalanjärvi sediment, di- and trichlorinated Aroclor 1242 congeners with less than two ortho chlorines and no double-para substitution were selectively removed at 20 °C (Hurme and Puhakka 1997). For example, PCBs assigned to chromatographic peaks no 4 (2-4-CB and 23-CB), 13 (25-4-CB), and 17 (23-4-CB) were all degraded in the laboratory tests. Nevertheless, the same peaks are present in sediment samples suggesting that the lower temperature, poor bioavailability, lack of

Fig. 4. PCB homolog distribution in Kernaalanjärvi sedmixtures.



oxygen, and the relatively low contaminant concentrations limit the *in situ* degradation of PCBs in sediments.

Reductive dechlorination

Microbial reductive dechlorination of PCBs does not remove the lower chlorinated PCBs but, on the contrary, increases the relative proportion of these congeners by replacing halogen substituents with hydrogen in higher chlorinated PCBs (Abramowicz 1990). In Kernaalanjärvi sediments, the in situ dechlorination of PCBs does not seem likely. A methanogenic enrichment culture from Kernaalanjärvi sediment dechlorinated Aroclor 1254 congeners assigned to peaks no. 35 (235-24-CB and 245-25-CB), 48 (245-34-CB), and 53 (245-245-CB) in laboratory experiments at 20 °C, but only after an enrichment period of 10 months (Hurme and Puhakka 1997). These congeners are major contaminants in all sediment samples, which together with long lag time indicates no in *situ* dechlorination. Furthermore, the overall sediment PCB concentrations at sites where *in situ* dechlorination has been detected have been considerably higher than in Kernaalanjärvi (Brown *et al.* 1987, Brown and Wagner 1990, Bedard and May 1996).

Toxicity of sediments

The toxicity of PCBs is usually presumed due to the presence of coplanar PCBs and some of their mono- and di-*ortho* substituted congeners (Safe 1990). The assessment of sediment toxicity based on total PCB content alone gives misleading results and thus a congener-specific analysis is always needed.

The concentrations of several mono- and diortho substituted coplanar congeners in Kernaalanjärvi sediment samples and their 2,3,7,8-TCDD toxic equivalents are given in Table 2. The most toxic PCB congeners, 345-345-CB and 345-34-CB, were not assigned to the Aroclor formula-

Table 2. Concentrations (mg kg⁻¹ d.w.) and 2,3,7,8-TCDD toxic equivalents (ng kg⁻¹ d.w.) of several non-, mono-, and di-*ortho* substituted coplanar PCBs in Kernaalanjärvi sediment samples (2–15 cm) and in Aroclor 1268 contaminated tidal creek sediment (Kannan *et al.* 1997).

		Conc. (mg kg ⁻¹ d.w.)/TEQ (ng kg ⁻¹ d.w.)				
IUPAC#	TEF ^{a)}	Site A	Site B	Site C	T.c.sed. ^{c)}	
77	0.0005	ND	ND	ND	1.7/0.9	
126	0.1	ND	ND	ND	0.8/82	
169	0.01	ND	ND	ND	0.2/1.8	
60 ^{b)}	0.001	57/57	7.9/7.9	4.0/4.0	12/12	
105 ^{b)}	0.0001	279/28	16/1.6	8.1/0.8	35/3.5	
118	0.0001	739/74	62/6.2	29/2.9	74/7.4	
156	0.0005	221/111	21/11	9.0/4.5	17/8.5	
128	0.00002	236/4.7	22/0.4	9.8/0.2	32/0.6	
137 ^{b)}	0.00002	28/0.6	3.5/0.1	2.3/0.0	17/0.3	
138	0.00002	413/8.3	67/1.3	34/0.7	131/2.6	
153	0.00002	526/11	70/1.4	29/0.6	138/2.8	
170	0.0001	57/5.7	17/1.7	10/1.0	32/3.2	
180	0.00001	56/0.6	12/0.1	6.5/0.1	114/1.1	
194	0.00002	ND	ND	ND	294/5.9	
Total TEQ (ng kg⁻¹ d.w.)		301	32	15	133	

ND = Not detected

^{a)} TEFs for IUPAC nos. 60, 128, 137, 138, 153, and 194 from Safe (1990), others from Ahlborg *et al.* (1994).

^{b)} Peak constitutes two equal congeners and the concentration is half the total peak concentration.

^{c)} Tidal creek sediment from Kannan *et al.* (1997).

tions, so their presence in sediment samples was not verified. Third non-*ortho* substituted coplanar PCB, 34-34-CB, coeluted with 236-34-CB in peak no 43, and was ignored. Table 2 compares our results with the corresponding values of tidal creek sediment (Glynn County, Georgia, USA) contaminated with residues of Aroclor 1268 from a study by Kannan *et al.* (1997). This site was chosen for comparison since the total sediment PCB content (9.6 mg kg⁻¹ d.w.) was similar to that of Kernaalanjärvi site A.

The estimated 2,3,7,8-TCDD toxic equivalents (TEQ) in Kernaalanjärvi sediment samples were between 15 and 301 ng kg⁻¹ d.w., whereas toxic concentrations in sediment quality guidelines range from 0.014 to 210 ng kg⁻¹ d.w. (Iannuzzi *et al.* 1995). Therefore, the PCB contaminated sediments likely pose a risk to organisms at least in the most contaminated parts of Kernaalanjärvi.

The sum concentrations of sediment PCBs in Kernaalanjärvi site A and in tidal creek sediment are at a same level, but the toxic equivalents differ considerably. This implies that the composition rather than the total amount of a PCB mixture determines its potential toxicity. The average chlorine content of PCB mixtures has also been used as a measure of product toxicity. In the tidal creek sediment, the chlorine content of PCBs was reported to average 64%, whereas in Kernaalanjärvi sediment samples it ranged from 54% to 56%.

Conclusions

The average contents of extractable PCBs in the 2–15 cm sediment layer in the most contaminated area of Kernaalanjärvi, the accumulation zone, and near the inflow of a noncontaminated river are 10.7, 1.2, and 0.53 mg kg⁻¹ d.w., respectively. Principal contaminant isomers in the sediment are pentachlorinated PCBs and, as compared to the discharge documentation, the minor relative proportion of lower chlorinated PCBs indicates selective removal of these congeners. Approximately 1 kg of PCBs exists momentarily in the water mass. Outflow, volatilization, and aerobic degradation are the principal processes that may have resulted in the removal of di-, tri-, and tetrachlorinated PCBs from the lake. *In situ* biodegra-

dation potential is limited, and volatilization is minor as compared to the proposed annual PCB outflow of 16 kg.

More information is needed on PCB concentrations in the water mass and in biota, before an overall fate estimation of PCBs in Kernaalanjärvi can be established. The distribution results of individual congeners are especially needed. The remaining PCBs in the sediment are more stable than the original PCB mixture because further dissolution is reduced. However, PCBs may still escape from the lake. The accumulation zone receives resuspended sediment material with sorbed PCBs until noncontaminated sediment covers the contaminated layers.

Toxicity risk of the PCB contaminated Kernaalanjärvi sediments was assessed as 2,3,7,8-TCDD toxic equivalents since total PCB content represents an insufficient indicator of toxicity. Considerable levels of several mono- and di-*ortho* substituted coplanar PCBs are present in sediment samples resulting in estimated 2,3,7,8-TCDD toxic equivalents between 15 and 301 ng kg⁻¹ d.w. with the highest value exceeding the sediment quality criteria reported by Iannuzzi *et al.* (1995).

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