Bioconcentration Factors (BCFs) of Specific Persistent Polychlorinated Bornane (Toxaphene) Congeners in Fish and Comparison with Bioaccumulation Factors (BAFs) of Biota from the Marine Environment

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Introduction

Polychlorinated bornanes are the main components of toxaphene which is produced by chlorination of camphene under UV light. Toxaphene is a complex mixture of at least 180 to 190 components, mostly with the formula $C_{10}H_{18-n}Cl_n$ or $C_{10}H_{16-n}Cl_n$ where n is 6–10 [1-4]. Toxaphene was first produced in the USA and became one of the most heavily used pesticide for several decades. The global usage of toxaphene from 1950 to 1993 has been estimated to be about 1.33 million tons[5]. This pesticide was banned in many countries (USA, Canada, Western Europe) due to its persistence and biological effects. However, it is still used in other countries. These chlorinated bornanes have been globally dispersed largely by atmospheric transport to the same extent as polychlorinated biphenyls (PCBs), DDT, lindane, and other hexachlorocyclohexanes[6,7]. Due to its long-range transport, stability, and high bioaccumulation potential toxaphene belongs to the persistent organic pollutants (POPs). Especially the polychlorinated bornanes are major contaminants in sediments, fish, marine mammals, human milk, and other biota.

However, in the course of examining these residues in biota it was noticed that their GC pattern was different compared to toxaphene standard[8-13]. Differences in GC pattern might be caused by photodegradation, selective bioaccumulation, and/or metabolism in aquatic and terrestrial organisms including humans[6-13]. Due to the differences in the toxaphene composition in environmental samples a precise toxaphene residue analysis requires the availability of pure chlorinated bornane indicator congeners. At this time the research group of H. Parlar succeeded in producing the 22 most important single congeners of toxaphene[14,15], which are commercially available from Ehrenstorfer (Augsburg, Germany) or Promochem (Wesel, Germany). About 25 chlorinated bornanes are regularly found in environmental samples. Most of the nona- and decachlorobornanes are normally absent, while many of the hexa- and heptachlorobornanes as well as some of the octa- and nonachlorobornanes are detected in sediments, fish and other biotic samples[11-18,24-29]. A study by Vetter et al.[18] showed that 11 polychlorinated bornanes were abundant in different seal species.

In this regard it is interesting to know the bioconcentration factors (BCFs) of these and other polychlorinated bornane congeners, which are regularly found in aquatic organisms. However, up to this time no bioconcentration tests with single congeners with fish or other aquatic organisms have been performed. The aim of this study was to predict bioconcentration factors of some relevant chlorinated bornanes in fish. Furthermore, the bioconcentration factors on a lipid basis (BCF_L) in fish were compared with bioaccumulation factors on a lipid basis (BAF_L) of two chlorinated bornane congeners determined in the aquatic environment.

Materials and Methods

The n-octanol/water partition coefficients (log K_{ow}) of the single chlorinated bornane congeners were calculated by means of the LOGKOW program of Meylan and Howard[20,21]. Furthermore, the log K_{ow} values were calculated on the basis of the measured log K_{ow} value of 5.28 for 1,2,3,4,7,7-hexachloro-2,5-norbornadiene which was determined by the HPLC method by Veith et al.[22]. By means of the quantitative structure-activity relationship (QSAR) of Mackay (eq. 1)

$$\log BCF_W = 1.00 \log K_{ow} - 1.32 \qquad (1)$$

the bioconcentration factors on a wet weight basis (BCF_W) of the chlorinated bornanes in fish were predicted. These BCF_W values refer to fish with a lipid content of ca. 5 % and were recalculated to bioconcentration factors on a lipid basis (BCF_L). Furthermore, the BCF values were compared with the bioaccumulation factors (BAFs) of Parlar No. 26 and No. 50 which were calculated by dividing the measured concentrations in zooplankton and different fish species from the aquatic environment[23] by the measured concentrations in the water.

Results and Discussion

The 7 most important persistent polychlorinated bornanes with their IUPAC name, Parlar numbers, different abbreviations, chemical structure, log K_{ow} and predicted bioconcentration factors (BCF_W and BCF_L) in fish are compiled in Table 1. The predicted BCF_L values of hepta-, octa- and nonachlorobornanes are between 600,000 and 71,000,000, and the predicted BCF_W values of these congeners in fish with 5 % lipid range from ca. 32,000 to 3,500,000. Furthermore, in Table 1 the BAF_W and BAF_L values of two polychlorinated bornane congeners (Parlar No. 26 and No. 50) are included which were calculated by the authors from the measured concentrations in zooplankton and different fish species and the water of a Canadian fresh water lake[23]. It is obvious that the BAF values of the chlorinated bornanes calculated from concentrations in aquatic organisms and water from the environment are by a factor between 1 and ca. 70 greater than the BCFs predicted from the log K_{ow} values. This can be explained in part by bioaccumulation and/or biomagnification.

Table 1. Chemical name, chemical structure, n-octanol/water partition coefficient (log K_{OW}), and predicted bioconcentration factors (BCFs) of 7 persistent Polychlorinated Bornanes with high bioconcentration potential. The measured log K_{ow} values and the measured BCFs of hexachloronorbornadiene and heptachloronorbornene are presented for comparison.

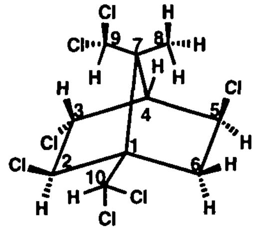
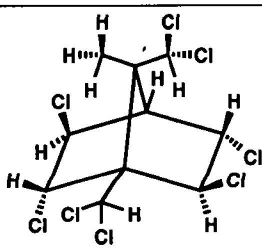
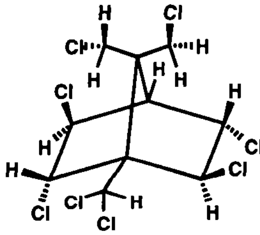
Chemical IUPAC name (Parlar No., No. of Andrews and Vetter, No. of Oehme, and other abbreviations)	Chemical structure	log K_{OW}	Bioconcentration factor (BCF) in fish and other aquatic organism	
			BCF_W[a]	BCF_L[b]
(±)-2-exo,3-endo,5-exo,9b,9c, 10a,10b-Heptachlorobornane (TOX 7, B7 - 1457[i])		5.80[c]	fish (lipid: 5 %) 31,500[g]	630,000[g]
		5.93[e]	43,000[g]	850,000[g]
(±)-2-endo,3-exo,5-endo,6-exo, 8b,8c,10a,10c-Octachloro-bornane (Parlar No. 26, TOX 8, T 2, B8 - 1413[i], 169-603[j])		5.98[c]	fish (lipid: 5 %) 48,000[g]	1,000,000[g]
		6.11[e]	65,000[g]	1,300,000[g]
			zooplankton (1.48 %) 163,000[h]	11,000,000[h]
			long-nose sucker (0.96 %) 133,000[h]	13,900,000[h]
			lake whitefish (2.69 %) 800,000[h]	30,000,000[h]
			lake trout (8.4 %) 5,660,000[h]	67,500,000[h]
(±)-2-endo,3-exo,5-endo,6-exo, 8b,9c,10a,10c-Octachloro-bornane (Parlar No. 40, B8 - 1414[i], 297 - 243[j])		6.05[c]	fish (lipid: 5 %) 56,000[g]	1,100,000[g]
		6.18[e]	76,000[g]	1,500,000[g]

Table 1 continued.

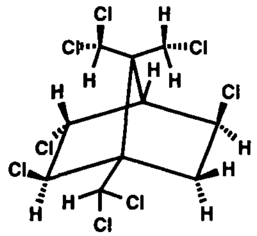
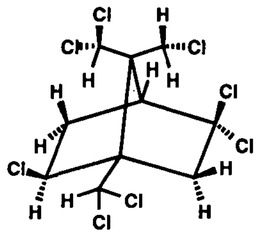
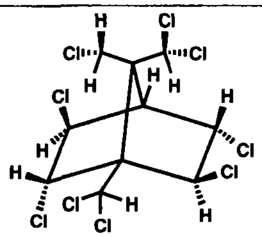
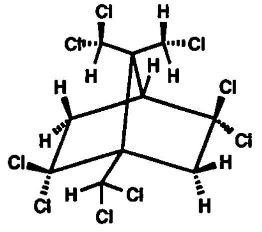
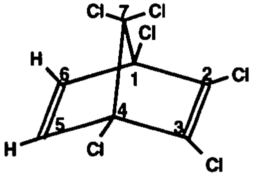
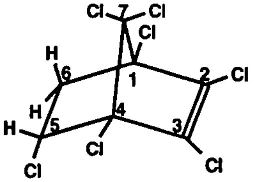
Chemical IUPAC name (Parlar No., No. of Andrews and Vetter, No. of Oehme, and other abbreviations)	Chemical structure	log K_{OW}	Bioconcentration factor (BCF) in fish and other aquatic organism	
			BCF_W[a]	BCF_L[b]
(±)-2-exo,3-endo,5-exo,8c,9b,9c,10a,10b-Octachlorobornane (Parlar No. 41, B8 - 1945[i], 41 - 643[j])		6.05[c] 6.18[e]	fish (5% lipid) 56,000[g] 76,000[g]	1,120,000[g] 1,500,000[g]
(±)-2-exo,5,5,8c,9b,9c,10a,10b-Octachlorobornane (Parlar No. 44, B8 - 2229[i], 97 - 643[j])		6.79[c] 6.92[e]	fish (5% lipid) 308,000[g] 420,000[g]	6,200,000[g] 8,300,000[g]
(±)-2-endo,3-exo,5-endo,6-exo,8b,8c,9c,10a,10c-Nonachlorobornane (Parlar No. 50, TOX 9, T12, Toxicant Ac, B9 - 1679[i], 297 - 303[j])		6.23[c] 6.36[e]	fish (lipid: 5 %) 85,000[g] 115,000[g]	1,700,000[g] 2,300,000[g]
			zooplankton (1.48 %) 290,000[h]	20,000,000[h]
			long-nose sucker (0.96 %) 100,000[h]	10,000,000[h]
			lake whitefish (2.69 %) 680,000[h]	25,000,000[h]
			lake trout (8.4 %) 650,000[h]	77,000,000[h]

Table 1 continued.

Chemical IUPAC name (Parlar No., No. of Andrews and Vetter, No. of Oehme, and other abbreviations)	Chemical structure	log K_{OW}	Bioconcentration factor (BCF) in fish and other aquatic organism	
			BCF$_W$ [a]	BCF$_L$ [b]
(±)-2,2,5,5,8c,9b,9c,10a,10b-Nonachlorobornane (Parlar No. 62, B9 - 1025[i], 99 - 643[j])		7.72[c] 7.85[e]	fish (lipid: 5 %) 2,630,000 [g] 3,500,000 [g]	 53,000,000 [g] 71,000,000 [g]
1,2,3,4,7,7-Hexachloro-2,5-norbornadiene; 1,2,3,4,7,7-Hexachlorobicyclo [2,2,1]hepta-2,5-diene (HCND)		5.15[c] 5.28[d]	fathead minnow (lipid: 4 %) 6,400 [f]	160,000
1,2,3,4,5,7,7-Heptachloro-2-norbornene; 1,2,3,4,5,7,7-Heptachloro-bicyclo [2,2,1]hept-2-ene (HepCNB)		5.55[c] 5.28[d]	fathead minnow (lipid: 4 %) 11,200 [f]	280,000

[a] BCF$_W$; Bioconcentration factor on a wet weight basis.

[b] BCF$_L$; Bioconcentration factor on a lipid basis.

[c] The log K_{OW} values were calculated using the LOGKOW Program of Meylan and Howard [20,21].

[d] The log K_{OW} value was measured by Veith et al. by the HPLC method [22].

[e] The log K_{OW} value was calculated on the basis of the measured log K_{ow} value of 5.28 for 1,2,3,4,7,7-hexachloro-2,5-norbornadiene.

[f] BCF$_W$ value in fathead minnows (0.12 g body weight, 4 % lipid) was measured in a 30-day flow-through test by Spehar et al. [31].

[g] BCF$_L$ value predicted from the log K_{OW} value.

[h] BCF data calculated from the concentration in biota and water of a Canadian fresh water lake measured by K. Kidd and D. Muir [23].

[i] Congener No. proposed by Andrews and Vetter [30a].

[j] Congener No. proposed by Oehme [30b].

In the future it is now possible to measure experimentally the K_{OW} values and also the BCF values of special chlorinated bornane congeners in fish and other aquatic organisms. However, it is necessary to use chlorinated bornane concentrations in the water which are below the water solubility of these very hydrophobic chemicals. Otherwise the BCF values are too low[33-36]. Furthermore, it is necessary to use the flow-through system and the kinetic approach.

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