Enantioselective determination of two major compounds of technical toxaphene in Canadian lake sediment cores from the last 60 years

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Introduction

Toxaphene is a complex mixture of bicyclic hydrocarbons. More than 16,000 congeners exist alone of the major substance class, i. e. polychlorinated bornanes [1]. 97% of the polychlorinated bornanes are chiral resulting in a total variety of 32,768 congeners [1]. Several hundred compounds were hitherto detected in technical products [2], and all of those which have been structurally elucidated were chiral. On high trophic level biota, only a few hepta-, octa- and nonachlorobornanes are accumulated while the bulk of the compounds of technical toxaphene (CTTs) is metabolized [3].
On the other hand, CTT residues in sediment were dominated by 2-*exo*,3-*endo*,6-*exo*,8,9,10-hexachlorobornane (Hx-Sed [4] or B6-923 [5]) and 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10-heptachlorobornane (Hp-Sed [4] or B7-1001 [5]. Stern et al. showed that these two CTTs approximately accounted for 60% of the total toxaphene concentration in the respective samples [5]. Miskimmin et al. described time profiles of toxaphene in sediment cores [6]. Since B6-923 and B7-1001 are chiral, the question arose whether these CTTs are accumulated in racemic composition and/or their formation/retention in sediments is accompanied with a change in the enantioratio (ER). In the present study sediment cores dated from 1935 to 1992 were analyzed. Electron-capture negative ionization mass spectrometry (ECNI-MS) and electron capture detection (ECD) was applied in combination with enantioselective gas chromatography using modified cyclodextrins. Three chiral stationary phases (CSPs) enantioseparated at least one of the persistent CTTs in lake sediment. One CSP has never before used for enantioseparation of CTTs. After set-up of the method the sediment cores were analyzed with respect to variations in the ER with time.

Experimental Methods

Origin and sample clean-up of the lake sediment samples

Sediment cores were from Hanson Lake, Canada. Sampling and sample clean-up were recently described in detail [6][7][8].

Enantioselective GC/MS method for B6-923 and B7-1001

Enantioseparations were performed on HP 5890 (Hewlett-Packard) gas chromatographs equipped with either ^{63}Ni electron capture detector (ECD) or electron-capture negative ionization mass spectrometry (ECNI-MS). The parameters were the same as recently described [3][9] except the ECNI-SIM masses which were m/z 307 and m/z 309 for hexachloro-CTTs (according to ref. [4]), m/z 343 and m/z 345 for heptachloro-CTTs, and m/z 377 and m/z 379 for octachloro-CTTs.

The following three CSPs were applied:

(i) A 30 m, 0.25 mm i. d. fused-silica capillary column, coated with 0.2 µm 25% *tert.*-butyldimethylsilylated ß-cyclodextrin diluted in 85% dimethyl, 15% diphenyl polysiloxane (BGB Analytik, Adliswil, Switzerland), hereafter abbreviated as ß-BSCD.

The GC oven program was the following: 80°C (1.5 min) 20°C/min to 180°C (15 min), 20°C/min to 200°C (15 min) 20°C/min to 230°C (15 min). Enantioseparations on ß-BSCD were performed with both GC/ECNI-MS and GC/ECD.

(ii) The second CSP consisted of 10% immobilized permethylated ß-cyclodextrin (CP-Chirasil-Dex, Chrompack, Middelburg), hereafter abbreviated as ß-PMCD. The GC oven program started at 120°C (1.5 min), followed by heating rates of 20°C/min to 150°C (25 min), 10°C/min to 200°C (10 min), and 10°C/min to 230°C (15 min). The ß-PMCD column was used with GC/ECNI-MS and GC/ECD.

(iii) The third CSP consisted of 35% heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-methyl)-ß-cyclodextrin diluted in OV1701 as recently described [10]. This CSP was installed in a gas chromatograph connected to ECD and only used for qualitative studies.

Quality control

GC/ECNI full scan mass spectra were recorded with ß-PMCD and ß-BSCD to exclude coelutions with other compounds. Reproducibility was studied on ß-BSCD in the selected ion monitoring mode: eight injections and quantitation of both m/z 343 and m/z 345 yielded a variation of ±0.02 for the ER which confirmed the accuracy of the method. Ten sediment extracts from Hanson Lake were injected into the GC/MS system by random selection (see below). Before every sediment sample, solvent blanks were performed to guarantee non-contaminated syringe, injector, GC column, and detector system.

Additionally, B7-1001 was isolated from the sediment core #6 by HPLC on a octadecylphase and elution with acetonitril/water (86/14, v/v). The pure heptachlorobornane was enantioseparated by GC/ECD on ß-PMCD confirming both the identity of the compound as well as the enantioratio determined by GC/MS (see below). Finally, selected cores were analyzed by GC/ECD to confirm the GC/MS findings.

Results and discussion

Figure 1 shows ECNI-MS chromatograms of the enantioseparation of B7-1001 and B6-923 on ß-PMCD and ß-BSCD.

Although enantioseparation of B6-923 failed on ß-PMCD, the enantiomers of B7-1001 were resolved (see Figure 1, left). ß-PMCD has not been successfully applied to enantioseparations of CTTs before [11]. Besides B7-1001, we also enantioseparated further CTTs on ß-PMCD [12]. Enantioseparation of B7-1001 was also obtained on ß-TBDM while the enantiomers of B6-923 kept unresolved.

Enantioseparation of both B7-1001 and B6-923 was obtained on ß-BSCD (see Figure 1, right). Interestingly, both compounds eluted in reversed order from ß-PMCD and ß-BSCD. On ß-PMCD, the non-resolved B6-923 enantiomers eluted prior to the resolved enantiomers of B7-1001 while ß-BSCD eluted the enantiomers of B6-923 after the enantiomers of B7-1001. Table 1 lists enantioratios (ERs) of B7-1001 and B6-923 determined in the respective sediment cores.

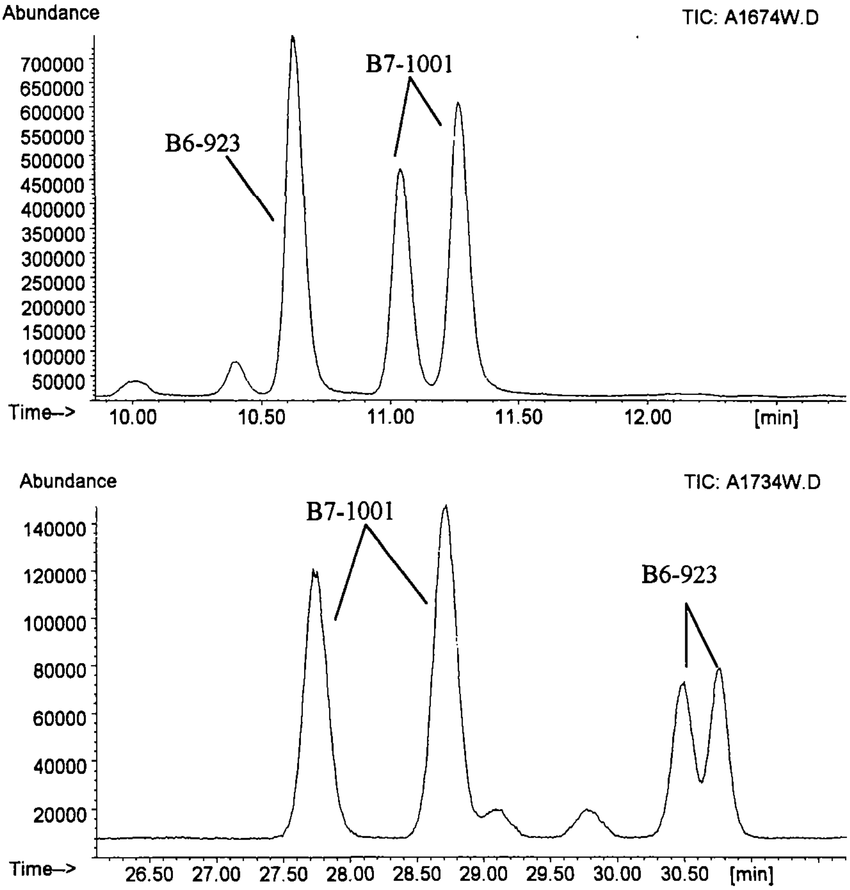

Figure 1: Enantioseparation of B7-1001 and B6-923 in Hanson Lake sediment cores
above: ß-PMCD
below: ß-BSCD

For B7-1001 we found a significantly enantioenriched second eluted enantiomer ranging from approx. 0.7 to 0.8. The values on both CSPs agreed very well with some deviations in cores #5 and #6 (see Table 1). On ß-BSCD, B7-1001 was interfered in core #3/4 by an unknown compound. This was confirmed by analysis with GC/ECD.

A trend towards lower enantioratios from the early to the most recent cores was found. So far, we have no explanation for this phenomenon.

The hexachlorobornane B6-923 (Hx-Sed) was racemic in all samples. No significant alteration in the enantioratio was observed. B6-923 was recently obtained from higher chlorinated bornanes by reductive dechlorination in soil under anaerobic conditions [13]. The authors only found one enantiomer. It was reported that enantioselective recristillazation might have occured with CTTs [13][14]. In the present sediment cores, however, both enantiomers were unequivocally detected in the respective samples in racemic composition. This also points to the conclusion that the type of microorganisms in the respective sediments might play an important role on the enantioselective breakdown of CTTs.

Table 1: Enantioratios (ERs) of B7-1001 and B6-923 in sediment from Hanson Lake

compound:	**B7-1001**	**B7-1001**	**B6-923**
	ß-PMCD	**ß-BSCD**	**ß-BSCD**
	ER (m/z 343 / m/z 345)	**ER (m/z 343 / m/z 345)**	**ER (m/z 307 / m/z 309)**
number (date)			
#2 (1992)	0.69 / 0.74	0.71 / 0.71	0.96 / 1.02
#3/4 (1984/7)	0.70 / 0.70	interfered*	0.99 / 1.01
#5 (1979)	0.68 / 0.70	0.77 / 0.76	0.98 / 1.00
#6 (1973)	0.72 / 0.71	0.78 / 0.78	0.98 / 0.98
#7 (1968)	0.75 / 0.75	0.81 / 0.80	0.98 / 1.00
#8 (1964)	0.81 / 0.81	0.82 / 0.82	1.06 / 1.03
#9 (1959)	0.79 / 0.79	0.82 / 0.84	0.97 / 0.97
#10 (1954)	0.81 / 0.81	0.81 / 0.82	1.01 / 1.02
#11 (1946)	0.79 / 0.79	0.80 / 0.78	1.00 / 0.99
#12 (1935)	0.77 / 0.77	< 1	0.97 / 1.02

* interference from an unknown compound was confimed by GC/ECD

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