

## LEVELS OF EIGHT TOXAPHENE CONGENERS IN DIFFERENT TISSUES OF MARINE ORGANISMS

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### Introduction

The organochloro pesticide toxaphene consists of more than 670 congeners [1]. In contrast, only a limited number of compounds of technical toxaphene (CTTs) is detected in end links of the marine food chain (e. g. marine mammals, birds and fish) [2][3]. Therefore, we suggested a standard with eight CTTs for toxaphene quantification in fish and marine mammals (see Table 1). Two of these congeners were isolated in our laboratory [4][5], while the other six CTTs are commercially available. Application of these six CTTs for quantification of toxaphene was also suggested by Kimmel et al. [8]. Three of the eight CTTs are used by German food chemists as indicator congeners to control toxaphene levels in fish and fish products [6][7]. In this study we determined the distribution of the 8 CTTs in several marine organisms (cod liver, blubber of seals and different tissues of Adelic penguins).

### Materials and Methods

**Standard solutions.** The structures and sources of the eight CTTs are given in Table 1.

**Table 1:** Systematic codes, Parlar numbers, chemical names and sources of the standard solutions of the eight CTTs (indicator congeners in bold type)

AV-Code [9]	Parlar-number [10]	Chemical name	Source of the standard solution
B7-1453	-	2- <i>exo</i> ,3- <i>endo</i> ,5- <i>exo</i> ,9,9,10,10-heptachlorobornane	1)
<b>B8-1413</b>	<b>P-26</b>	<b>2-<i>endo</i>,3-<i>exo</i>,5-<i>endo</i>,6-<i>exo</i>,8,8,10,10-octachlorobornane</b>	<b>2)</b>
B8-1412	-	2- <i>endo</i> ,3- <i>exo</i> ,5- <i>endo</i> ,6- <i>exo</i> ,8,8,9,10-octachlorobornane	3)
B8-1414	P-40	2- <i>endo</i> ,3- <i>exo</i> ,5- <i>endo</i> ,6- <i>exo</i> ,8,9,10,10-octachlorobornane	2)
B8-1945	P-41	2- <i>exo</i> ,3- <i>endo</i> ,5- <i>exo</i> ,8,9,9,10,10-octachlorobornane	2)
B8-2229	P-44	2- <i>exo</i> ,5,5,8,9,9,10,10-octachlorobornane	2)
<b>B9-1679</b>	<b>P-50</b>	<b>2-<i>endo</i>,3-<i>exo</i>,5-<i>endo</i>,6-<i>exo</i>,8,8,9,10,10-nonachlorobornane</b>	<b>2)</b>
<b>B9-1025</b>	<b>P-62</b>	<b>2,2,5,5,8,9,9,10,10-nonachlorobornane</b>	<b>2)</b>

- 1) Solution calibrated with GC/FID after isolation from Melipax [4] (not commercially available)  
 2) Toxaphen-Mix 3 from Dr. Ehrenstorfer (Augsburg, Germany)  
 3) Solution calibrated with GC/FID after isolation from seal blubber [5] (not commercially available)

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**Sample clean-up.** The sample clean-up including all chemicals was earlier described in detail [11]. Before quantification of the CTTs, PCBs and further aromatic organochlorines were separated on 8.0 g activated silica [12][13]. The origin of the samples is given in Table 2.

**GC/ECD measurements.** A HP 5890 II gas chromatograph (Hewlett-Packard) equipped with two <sup>63</sup>Ni electron capture detectors (ECD) was applied. Two capillary columns, a CP-Sil8/20% C18 and a CP-Sil2 (both 50 m, 0.25 mm i.d., 0.25 µm film thickness; Chrompack, Middelburg, The Netherlands), were installed in the GC oven. The injector and detector temperatures were set at 250°C and 300°C, respectively. Two different oven programmes were used: 1. (1.2 bar column head pressure, carrier gas: helium) 60°C (1.5 min), 40°C/min to 180°C (2 min), 2°C/min to 230°C (25 min), 10°C/min to 270°C (15 min); 2. (1.7 bar helium) 60°C (1.5 min), 15°C/min to 180°C (40 min), 25°C/min to 230°C (20 min), 15°C/min to 270°C (15 min).

## Results and Discussion

Table 2 shows levels of eight CTTs in the analyzed tissues of different marine organisms. In all samples the indicator congeners B8-1413 (P-26) and B9-1679 (P-50) were among the three highest concentrated CTTs, where as the third indicator compound B9-1025 (P-62) was found in position 2 to 6 within the eight CTTs. Particularly low levels of B9-1025 (P-62) relative to B9-1679 (P-50) were determined in Weddell seals and harp seals. Another congener, B8-2229 (P-44), was often higher concentrated than B9-1025 (P-62) (see also Figure 1).

B8-1412, which was isolated from seal blubber [5] and which is not available as standard solution, was also high abundant in the samples. Particularly, in tissues of two Adelie penguins, B8-1412 reached the second highest level of the eight CTTs (see Figure 1d). B8-1412 is identical with a major abundant chlorobornane in Arctic water and air [14].

B8-1413 (P-26) and B9-1679 (P-50) dominated the CTT pattern of seal blubber. However, the dominance of these two congeners was more pronounced in Antarctic Weddell seals than in grey seals from Iceland (see Figure 1a and 1b). This is in agreement with an earlier study of Antarctic seals [2].

In addition to cod livers from the Baltic Sea and Iceland, we also determined the eight CTTs in cod liver oil SRM 1588 (see Figure 1c). There was a clear tendency towards higher chlorinated bornanes in SRM 1588 in comparison with cod livers from the Baltic Sea. Particularly, B9-1025 (P-62) and B9-1679 (P-50) were more abundant in SRM 1588 (see Figure 1c).

The remaining three CTTs, B7-1453, B8-1414 (P-40), and B8-1945 (P-41), were mostly lower concentrated than the other five chlorobornanes. B7-1453 is, however, the only heptachlorobornane which could be quantified in the samples.

## Conclusions

These results show that it is quite possible that other CTTs are equal or higher concentrated than the indicator CTTs B8-1413 (P-26), B9-1679 (P-50), and B9-1025 (P-62) or even the commercially available CTTs. Furthermore, the comparison of toxaphene levels in the literature is difficult: depending on the number of congeners used for the quantitation, significantly different toxaphene levels will be obtained. Problems also arise if toxaphene is quantified relative to the technical mixture. We suggest to quantify toxaphene on a congener-specific basis. The application of as many as possible CTT standards for quantitative studies is recommended. However, there is still a need for making more toxaphene compounds (e. g. B8-1412) commercially available.

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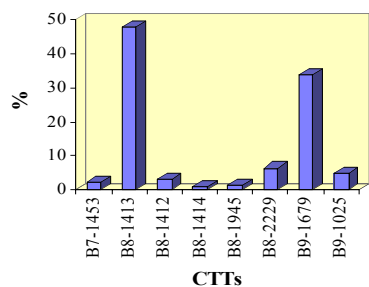
Table 2: Levels of eight CTTs [ $\mu\text{g}/\text{kg}$ ] in tissues of marine organisms of different origin (indicator congeners in bold type)

Species	Origin	Tissue	n	B7-1453 (-)	B8-1413 (P-26)	B8-1412 (-)	B8-1414 (P-40)	B8-1945 (P-41)	B8-2229 (P-44)	B9-1679 (P-50)	B9-1025 (P-62)	$\Sigma\text{CTT-8}$
Seal <i>hoerus</i> )	Rügen, Baltic Sea	blubber	1	43	<b>222</b>	38	17	45	102	<b>221</b>	<b>45</b>	733
Seal <i>hoerus</i> )	Faxaflói, Western Iceland	blubber	6	2 <sup>3)</sup> (2-3) <sup>4)</sup>	<b>10</b> (7-16)	5 (3-8)	2 (1-4)	3 (2-4)	8 (6-11)	<b>13</b> (8-20)	<b>6</b> (2-11)	48 (32-77)
Seal <i>indica</i> )	North Sea	blubber	1	61	<b>381</b>	74	27	27	162	<b>697</b>	<b>28</b>	1457
Seal <i>nychotes</i> <i>alli</i> )	Weddell- Sea <sup>1)</sup> , Antarctic	blubber	3	6 (4-8)	<b>182</b> (76-247)	12 (5-20)	3 (1-4)	5 (3-6)	24 (12-31)	<b>130</b> (52-173)	<b>17</b> (8-25)	378 (161-489)
Seal <i>cephalus</i> <i>i</i> )	Jubany <sup>2)</sup> , Antarctic	blubber	1	0.4	<b>3.6</b>	0.8	0.3	0.1	0.8	<b>1.6</b>	<b>0.8</b>	8.4
Seal <i>inga</i> <i>a</i> )	Jubany <sup>2)</sup> , Antarctic	blubber	1	0.1	<b>2.2</b>	0.4	0.1	0.1	0.3	<b>1.0</b>	<b>1.1</b>	5
Penguin <i>celis</i> <i>2)</i>	Jubany <sup>2)</sup> , Antarctic	brain	1	n.d. <sup>5)</sup>	<b>1.9</b>	1.2	n.d.	n.d.	0.4	<b>0.8</b>	<b>n.d.</b>	4
Penguin <i>celis</i> <i>2)</i>	Jubany <sup>2)</sup> , Antarctic	liver	1	0.1	<b>1.9</b>	1.3	0.1	0.1	0.7	<b>1.1</b>	<b>0.3</b>	6
Penguin <i>celis</i> <i>2)</i>	Jubany <sup>2)</sup> , Antarctic	fat	1	1.2	<b>34</b>	23	1.2	0.7	2.8	<b>23</b>	<b>12</b>	98
Penguin <i>celis</i> <i>2)</i>	Jubany <sup>2)</sup> , Antarctic	liver	1	0.03	<b>0.4</b>	0.3	n.d.	n.d.	n.d.	<b>0.1</b>	<b>0.1</b>	0.8
Seal <i>morhua</i> )	Iceland	liver	3	2 (2-3)	<b>15</b> (10-18)	7 (6-9)	8 (6-9)	4 (3-4)	11 (11-12)	<b>28</b> (20-35)	<b>12</b> (10-14)	87 (68-102)
Seal <i>morhua</i> )	Baltic Sea	liver	5	12 (8-15)	<b>59</b> (35-83)	14 (7-20)	9 (3-16)	12 (6-17)	31 (21-40)	<b>68</b> (31-88)	<b>17</b> (8-41)	222 (127-303)
Seal <i>morhua</i> )	SRM 1588 <sup>6)</sup>	liver oil	1	25	<b>248</b>	60	24	37	126	<b>393</b>	<b>281</b>	1194

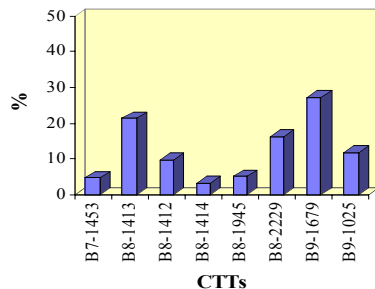
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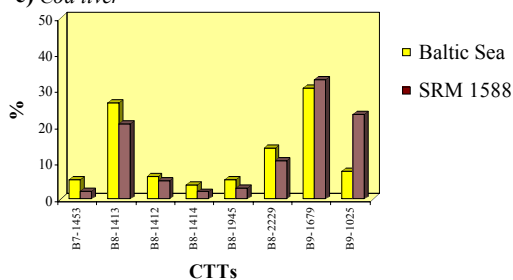
a) Weddell seals, Antarctic (n = 3)



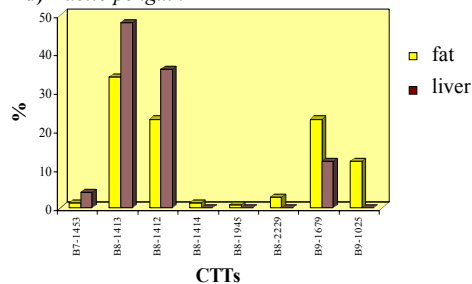
b) Grey seals, Iceland (n = 6)



c) Cod liver



d) Adelie penguin



e 1: Percental distribution of eight CTTs determined in several marine organisms

## ences

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