Determination of polychlorinated terphenyls in biota and sediments with gas chromatography/mass spectrometry

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Abstract

An analytical method for the determination of polychlorinated terphenyls (PCTs) in environmental samples using gas chromatography/mass spectrometry with negative chemical ionisation has been developed. Concentrations of PCTs have been determined in biota and sediments and mainly tetra-decachloroterphenyls were detected. PCT concentrations in biota ranged from 0.3-7,400 µg/kg wet weight of which 50-70% was related to hexa- and heptachloroterphenyls. Application of different calculation methods influenced the final results. Total PCT-concentrations come to approximately 4% of the total PCB-concentrations in biota and 10-15% in sediments.

Introduction

The production of PCTs was started together with that of PCBs in 1929 by Monsanto Chemical Company in the USA [1,2]. Since then, PCTs have been produced in the USA, France, Italy, Germany and Japan [2,3]. The total production is estimated at 60,000 metric tons [2,3]. Most manufacturers have stopped their PCT-production since the 1970s [2]. Brand names of the technical PCT mixtures are often similar to those of PCBs, but numerical codes are different. For example Aroclor 12.. stands for a PCB mixture, while Aroclor 54.. stands for a PCT mixture. Technical applications of PCTs are also very similar to those of PCBs. According to Jensen and Jørgensen [2] the toxicity of PCTs is considered to be equivalent to that of PCBs, although less information is available on PCTs.
Reports on the presence of PCTs in the environment are scarce and often limited to studies with packed column gas chromatography (GC) with electron capture detection[1,4]. Only Hale et al. (1990) [5] reported PCTs in sediments and shellfish in a more recent study carried out with capillary GC. We have developed a method with GC/mass spectrometry with negative chemical ionisation (NCI-MS) for the determination of PCTs in environmental samples, and determined PCT concentrations in biota and sediments. Different calculation methods and

comparisons with different Aroclor mixtures were evaluated in order to improve the reliability of the data.

Materials and method

All fish samples were pooled samples of 25-50 specimens, caught in 1990-1992. Cormorant livers were obtained from Rijkswaterstaat-Flevoland Division, the Netherlands and tufted duck eggs and sheldrake eggs were obtained from Rijkswaterstaat Dordrecht, the Netherlands. Two blubber samples were taken from a white beaked dolphin and a harbour porpoise, kindly supplied by Dr. R. Kastelein of the Marine Mammal Park, Harderwijk, the Netherlands. Muscle and liver samples of the penguin were carefully dissected by personnel of the Zoological Museum of Amsterdam.

From all biota samples an amount of tissue was homogenized, ground with sodium-sulphate, and soxhlet-extracted with dichloromethane/n-pentane (1:1) for 12 h. The dichloromethane was evaporated and the fat was removed by sulphuric acid. Subsequently the extract was cleaned-up on alumina and fractionated on silica. 1,2,3,4-Tetrachloronaphthalene was added as an internal standard and the extract was concentrated to 200 µl. Recoveries range 88-94%. The determination of PCTs was carried out on an HP 5988A GC/MS using NCI under the following conditions:

Column:	CP-Sil 12, 45 m x 0.25 mm, film thickness 0.20 µm, carrier gas: He, 100 kPa
Injection:	splitless, temperature: 295°C, splitter closing time: 2.5 min
GC oven program:	3 min 90°C, 30°C/min - 210°C, 3.5°C/min - 280°C, 53 min 280°C, post run: 20 min 290°C
Source temperature:	100°C, transferline temperature: 290°C
Ionisation gas:	methane, source pressure: 1 torr
Scanned ions:	m/z 332,334 (tri CT), 366,368 (tetra CT), 400,402 (penta CT), 436,438 (hexa CT), 470,472 (hepta CT), 504,506 (octa CT), 538,540 (nona CT), 264,266 (TCN)

Results and discussion

NCI was prefered to electron impact as ionisation method because of a higher sensitivity. Only the lower chlorinated terphenyls (≤ 4 chlorine atoms) showed lower sensitivity with NCI. However, lower chlorinated terphenyls are hardly present in the A5442 mixture and even less in A5460. NCI spectra show mainly $[M]^-$, $[M-Cl+H]^-$ and $[M-Cl_2+H_2]^-$ fragments, while the EI spectra are characterized by abundant fragmentation and the occurrence of double charged fragments.

Table 1 shows the results of the PCT determinations in biota and sediments. For comparison the CB 153 and total PCB concentrations in the same samples have also been given. PCT concentrations in biota come to approximately 4% of the total PCB concentrations in the same samples. This percentage is similar to that of the production figures: the PCT production is about 4% of that of PCBs. This would mean that PCBs and PCTs show a comparable environmental behaviour. The sediment samples, however, contain a relatively higher percentage of PCTs: 10-15 % of the PCB concentration. Sediments contain more higher chlorinated PCTs, but they still resemble Aroclor 5442 more than Aroclor 5460.

Table 1 PCT concentrations in biota and sediments expressed in µg/kg wet weight (A 5442), together with the corresponding CB 153 and total PCB concentrations.

species	location	year	fat/ orgC g/kg	PCT µg/kg[3]	PCB µg/kg[3]	CB153 µg/kg[3]	PCT/ PCB %
Eel *(Anguilla anguilla)*	Rhine (Lobith)	1992	117	210	4,900	510	4.3
Eel *(Anguilla anguilla)*	Nieuwe Merwede	1992	172	160	6,700	740	2.4
Eel *(Anguilla anguilla)*	Haringvliet-east	1992	118	140	5,300	960	2.7
Eel *(Anguilla anguilla)*	Meuse (K. veer)	1991	141	130	3,800	560	3.4
Eel *(Anguilla anguilla)*	Roer (Vlodrop)	1992	192	100	4.000	330	2.5
Eel *(Anguilla anguilla)*	Yssel Lake	1992	260	52	910	130	5.7
Eel *(Anguilla anguilla)*	Ketelmeer	1992	192	84	1,900	250	4.5
Eel *(Anguilla anguilla)*	Lauwersmeer	1992	138	6	180	19	3.3
Pike perch *(Stizostedion lucioperca)*	Hollandse Yssel	1990	9	5	280	210	1.8
Cod[1] *(Gadus morhua)*	Dutch coast	1992	513	420	5,600	1,100	7.4
Cod [1] *(Gadus morhua)*	north. North Sea	1992	528	43	440	47	9.9
Plaice *(Pleuronectus platessa)*	North Sea	1990	10	1	10	0.82	12
Herring *(Clupea harengus)*	Dutch coast	1990	172	3	130	14	2.1
Twaite shad *(Alosa fallax)*	Dutch coast	1991	78	13	590	74	2.2
Whitebeaked dolphin[1] *(Lagenorynchus albirostris)*	North Sea	1991	53	380	16,000	2,400	2.3
Harbour porpoise[2] *(Phoceana phoceana)*	North Sea	1990	806	1,900	71,000	15,000	2.7
Gentoo penguin [1] *(Phygoscelis papua)*	Falkland Islands	1991	53	1.4	24	2.0	5.8
Sheldrake egg (*Tadorna tadorna*)	Prinsseseplaat	1991	182	56	7,600	1,130	0.7
Tufted duck egg (*Aythya fuligula*)	Zoommeer	1991	173	35	1,100	100	3,0
Cormorant[1] (*Phalacrocorax carbo*)	Ketelmeer	1990	40	120	3,700	600	3.2
Cormorant[1] (*Phalacrocorax carbo*)	Ketelmeer	1990	34	92	2,500	480	3.7
Sediment	Rhine (Lobbith)	1992	46	130	870	60	15
Sediment	Haringvliet-east	1992	27	36	350	25	10
Sediment	Meuse (K.veer)	1992	43	87	580	42	15

[1]: liver, [2]: blubber,other samples: fillet (muscle); [3]: in sediment: on dry weight basis; n.a.: not analyzed

Table 2 PCT concentrations in biota, calculated by different methods (µg/kg wet weight).

sample	TIC A5442	TIC A5460	m/z=436 A5442	m/z=470 A5442	m/z=470 A5460	m/z=506 A5442	m/z=506 A5460
Cod liver, southern North Sea	420	300	490	2200	440	1300	26
Cod liver, northern North Sea	43	31	42	180	33	140	2.3
Eel fillet, Roer Vlodrop	100	72	110	600	120	650	13
Eel fillet, Haringvliet East	140	100	180	860	170	610	12
Eel fillet, lake IJssel	52	37	63	300	58	240	4.3
Tufted duck egg, Zoommeer	35	25	32	140	26	110	2.0
Whitebeaked dolphin, North Sea	7400	5500	9640	42000	8600	19000	370

PCT concentrations in eel from the Yssel Lake are 2-fold lower than those reported by Freudentahl and Greve (1973)[4] in Yssel Lake eel from 1971 . Regarding the analytical uncertainties, this difference is not significant. Clearly PCT levels in biota are on a lower level than PCBs. However, concentrations higher than 7 mg/kg wet weight in dolphin show that PCTs do have an environmental significance. The PCT-level in biota is roughly comparable to that of total-DDT. Similar to PCBs, PCT

levels in cod liver from the southern North Sea are higher than those in northern North Sea cod liver.
This is the first report of the presence of PCTs in sub-Antarctic organisms, which shows that the global distribution of PCTs is comparable to that of PCBs.
PCT concentrations in Table 1 are based on comparison of total ion chromatograms (TICs) of the samples with those of A5442. However, when instead of A5442, A5460 is used or when data based on comparison of specific m/z ratios are used, different PCT concentrations may be calculated. This is shown in Table 2. In order to find the most reliable result, a technical mixture with the closest resemblance to the PCT pattern of the sample as a standard is suggested. The fish samples and other biota in this study contained mainly hexa and hepta-CTs, about 50-70%. The resemblance with A5442 was therefore better than with A5460. TICs are to be preferred to single m/z ratios because fragments of higher chlorinated terphenyls may interfere with lower chlorinated PCT fragments. Besides, concentrations of e.g. hexa or hepta-CTs in Aroclor mixtures are unknown and coverage of the complete pattern in a TIC may provide a stronger basis for the final concentrations.

Conclusions

GC/NCI-MS is a suitable and sensitive detection method for PCTs with more than four chlorine atoms. PCTs have been found in environmentally significant concentrations in fish, sediments and waterbirds and their eggs from the Netherlands, in North Sea fish and marine mammals, and in penguins from the Falkland Islands. PCT concentrations in biota were related for 50-70% to hexa and hepta CTs. PCT levels in biota come to approximately 4% of the PCB levels in the same samples and were roughly comparable to total-DDT levels. In sediments relatively higher PCT concentrations are found, approximately 10-15 % of PCB levels. For calculation of PCT concentrations a comparison of the total ion chromatogram of a sample with that of a technical mixture that has the best resemblance with the pattern in the sample is suggested.

References

1. Jamieson, J.W.S. Polychlorinated terphenyls in the environment. Ottawa, Ontario, Canada: Environmental Protection Service, 1977, report EPS-3-EC-77-22.
2. Jensen, A.A., Jørgensen, K.F. Polychlorinated terphenyls (PCTs) use, levels and biological effects. *Sci. Total. Environ.* 1983; 27: 231-250.
3. Kok, A. de, Geerdink, R.B., de Vries, G., Brinkman, U.A.T. An evaluation of chromatographic methods for the analysis of polychlorinated terphenyls in environmental samples. *Intern. J. Environ. Anal. Chem.* 1982; 12: 99-122.
4. Freudenthal, J., Greve, P.A. Polychlorinated terphenyls in the environment. *Bull. Environ. Contam. Toxicol.* 1973; 10: 108-111.
5. Hale, R.C., Greaves, J. Gallagher, K. Vadas, G.G. Novel chlorinated terphenyls in sediments and shellfish of an estuarine environment. *Environ. Sci. Technol.* 1990; 24: 1727-1731.