Determination of Polychlorinated Terphenyls in Aquatic Biota and Sediment with Gas Chromatography/Mass Spectrometry Using Negative Chemical Ionization

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Polychlorinated terphenyls (PCTs) have been determined in aquatic biota and sediments by gas chromatography/mass spectrometry using negative chemical ionization. The use of various methods of calculation is discussed. Total PCT concentrations expressed as A (Aroclor) 5442 equivalents ranged from 0.28 to 7400 μg/kg of wet weight in biota, with hexachloroterphenyls (hexa-CTs) as the major group of CTs present. In sediments, total PCT concentrations expressed as A5442 equivalents ranged from 22 to 100 μg/kg of wet weight, with hepta-CTs as the dominant group of congeners. Total PCT concentrations in biota were approximately 1−10% of total polychlorobiphenyl (PCB) concentrations and in sediments 10−25% of total PCB concentrations. The rather unexpectedly high concentrations of PCTs, especially in the sediment samples, should stimulate further research on their general environmental distribution.

Introduction

The attention devoted to the environmental presence of polychlorinated terphenyls (PCTs) has always been very limited compared to polychlorobiphenyls (PCBs) (*1*−*5*). The production of both PCTs and PCBs was started in 1929 in the United States by Monsanto Chemical Co. Since then PCTs have also been produced in France, Italy, Germany, and Japan (*6*). Information about production volumes is incomplete, but during the period 1955−1980, ∼60 000 metric tonnes were produced worldwide (*6*, *7*), which is 15−20-fold lower than the total PCB production during that period (*8*) or the cumulative worldwide PCB production till 1984. Table 1 contains information about producers, countries, and brand names (*7*). Monsanto USA voluntarily terminated the production in 1972. In Germany the production of PCTs was terminated in 1974, in Italy in 1975, and in France in 1980 (*6*). No information is available about the production stop of PCTs in Japan. PCTs are, or were, commercially available as technical mixtures under different brand names which are often similar to those of PCB mixtures (Table 1). In the Aroclor series, PCB/PCT mixtures like the A60 series, which consisted of mixtures of A5460 and A1221 (*9*), were also available. PCTs are used for essentially the same purposes as PCBs: in waxes (Rigidax) (*6*), printing inks, paints, lacquers, and electronic equipment and as hydraulic fluids (Pydraul) (*6*), lubricants, plasticizers, and fire retardants.

PCTs have chemical and physical features closely resembling those of PCBs (*8*, *9*). Information on the toxicological properties of PCTs is rather scarce. Literature data indicate that the toxic effects of PCTs are comparable to those of PCBs, although some authors described the effects as less severe (*6*, *10*). Until now, no attention has been paid to the relation between the structure of PCT congeners and their specific toxicity. Although PCTs have been determined in fish, oysters, birds, wild dogs, cats, snakes, cow livers, pigeon fat, mother's milk, human fat/blood, soil, sediment, garbage, and river water (*7*) (*cf.* Table 2), compared with PCBs, much less information is available on environmental levels of PCTs. This should be of some concern because, on the basis of the production figures quoted above, environmental contamination/distribution of PCTs may well be wider than is generally assumed.

PCT mixtures are very complex because of the possible ortho, meta, and para position of the third phenyl ring (Figure 1). The theoretical number of congeners is 8149 (*11*). As a result, an unambiguous separation of all congeners is impossible even by multidimensional gas chromatography. Further, chemical transformations in the environment, biological availability, uptake kinetics, metabolism, and elimination from organisms will influence the PCT pattern in samples. Combined with the lack of commercial availability of most individual PCT congeners, these aspects make accurate quantification of PCTs very difficult. Chittim et al. (*12*) synthesized 22 PCT congeners, but these were all lower chlorinated terphenyls (mono−penta). Therefore, PCTs are quantified as total PCT using technical mixtures such as A5442, A5460, or Clophen-Harz W as standards, either on the basis of selected ions by using gas chromatography/mass spectrometry (GC/MS) with electron impact (EI) or negative chemical ionization (NCI) or by using the same techniques, on the basis of "total ion", assuming equal response factors for all congeners or by GC/electron capture detection (ECD) (*7*). Actually, at present such semiquantitative analysis is the best possible option.

The relatively poor analytical approach based on calculation of Aroclor equivalents is a general problem in the analysis of complex mixtures like PCTs, PBBs (*13*), chlorinated camphenes (toxaphene) (*14*), and chlorinated paraffins (*15*). The usefulness of GC/NCI-MS for the determination of chlorinated paraffins has been demonstrated (*15*, *16*). Further improvements may be expected from the use of hyphenated techniques, especially a combination of multidimensional GC and NCI-MS, and congener-specific analyses.

In the present study, we have used GC/NCI-MS for the determination of PCTs in aquatic biota and sediments,

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TABLE 1

Producers and Brand Names of PCTs (*7*)

producer	country	brandname
Monsanto	USA	Aroclors 5432, 5442, and 5460
Kanegafuchi	Japan	Kanechlor C
Mitsubishi-Monsanto	Japan	Aroclor series
Bayer	Germany	Leromolls 112-90 and 141 Clophen-Harz W
Caffaro	Italy	Cloresils A, B, and 100
Prodelec	France	Phenoclor, Electrophenyl T-60
?	France	Terphenyl Chlore T60

TABLE 2

Selected Literature Data on PCT Concentrations in Environmental Samples

sample and location	concn (μg/kg)	basis of calcn[a]	standard	ref
sediment, James River, USA 1989	26000	dw	A5460	19
oyster, Eastern Scheldt, The Netherlands 1971	150	lw	*m/z* 436 Clophen-Harz W	25
oyster, Eastern Scheldt, The Netherlands 1971	80	lw	*m/z* 470 Clophen-Harz W	25
eel, Yssel Lake, The Netherlands 1971	500	lw	*m/z* 436 Clophen-Harz W	25
eel, Yssel Lake, The Netherlands 1971	200	lw	*m/z* 470 Clophen-Harz W	25
sparrowhawks, herons, England 1976	50−1200	ww	A5460	27
oysters, Chesapeake Bay, USA 1988/1989	<400−35000	dw	A5432	10
sediment, Chesapeake Bay, USA 1988/1989	<5−250000	dw	A5432	10
grey seal, Sweden 1976	500−1000	dw	perchlorination	24
white-tailed eagle, Sweden 1976	2800−17200	lw	perchlorination	24
trout, Soca River, Yugoslavia 1977	3−8	ww	A5460	28
herring eggs, Bay of Fundy, Canada 1972	100	ww	A5460	23
herring fat, Bay of Fundy, Canada 1972	1400	lw	A5460	23
cormorant eggs, Bay of Fundy, Canada 1972	nd[b]	ww	A5460	23
sediment coastal area, Bay of Biscay, Spain 1986/1987	0−0.4	ww	Leromoll 141	20

[a] lw, lipid weight; dw, dry weight; ww, wet weight. [b] Not detected.

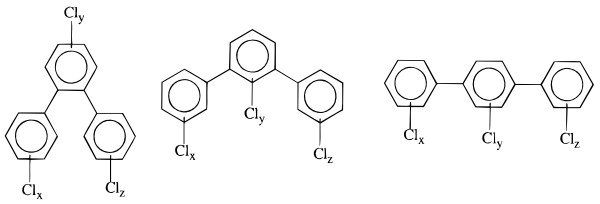

FIGURE 1. Ortho-, meta- and para-PCTs, $C_{18}H_{14-n}Cl_n$, with $1 \leq n = x + y + z \leq 14$.

especially because the sensitivity offered by this technique cannot be obtained by the use of GC/ECD or GC/EI-MS. Different methods of calculation and the comparison of real-life PCT patterns with those of different Aroclor mixtures were studied in order to improve the reliability of the data.

Materials and Methods

All fish and sediment samples were collected by the Netherlands Institute for Fisheries Research. Cormorant livers and tufted duck and sheldrake eggs were obtained from Rijkswaterstaat—Flevoland Division, The Netherlands, and Rijkswaterstaat Dordrecht, The Netherlands, respectively. The sampling locations in the Dutch inland waters are indicated in Figure 2. The harbor porpoise (male, age >10 years) and whitebeaked dolphin (male, age 10 years) samples were gifts from Dr. R. A. Kastelein of the Marine Mammal Park, Harderwijk, The Netherlands. The penguin was found in the net of a Dutch fishing vessel, fishing near the Falkland Islands in May 1991. Muscle and liver samples were carefully dissected by technicians of the Zoological Museum of Amsterdam.

Fish samples consisted of a number of individual fishes, from which equal quantities of the required tissue were pooled. Sediment samples consisted of 10 subsamples taken from within an area of 1000 m^2. After thorough

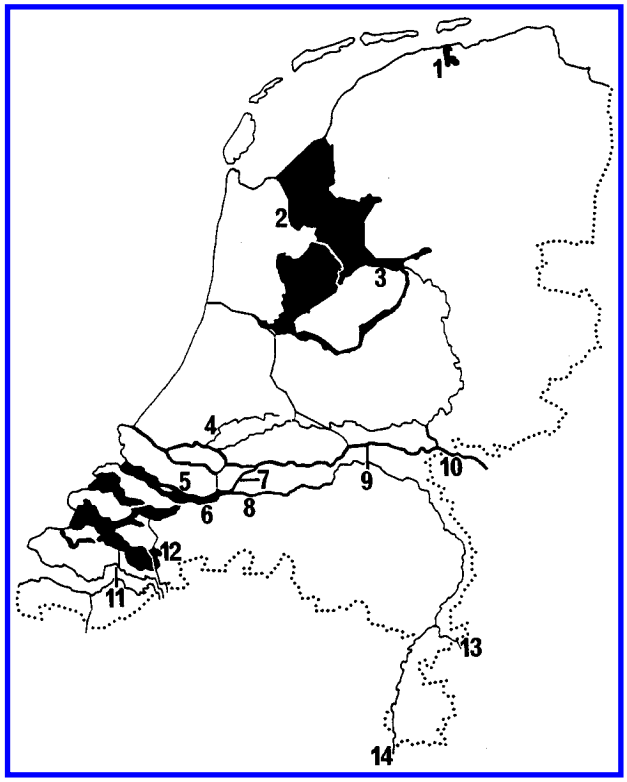

FIGURE 2. Sampling locations in Dutch inland waters: (1) Lauwersmeer, (2) Yssel Lake, (3) Ketelmeer, (4) Hollandse Yssel (Gouderak), (5) Haringvliet-east, (6) Hollands Diep, (7) Nieuwe Merwede, (8) Meuse (Keizersveer), (9) Waal (Tiel), (10) Rhine (Lobith), (11) Western Scheldt, (12) Zoommeer /Prinsesseplaat, (13) Roer (Vlodrop), and (14) Meuse (Eijsden).

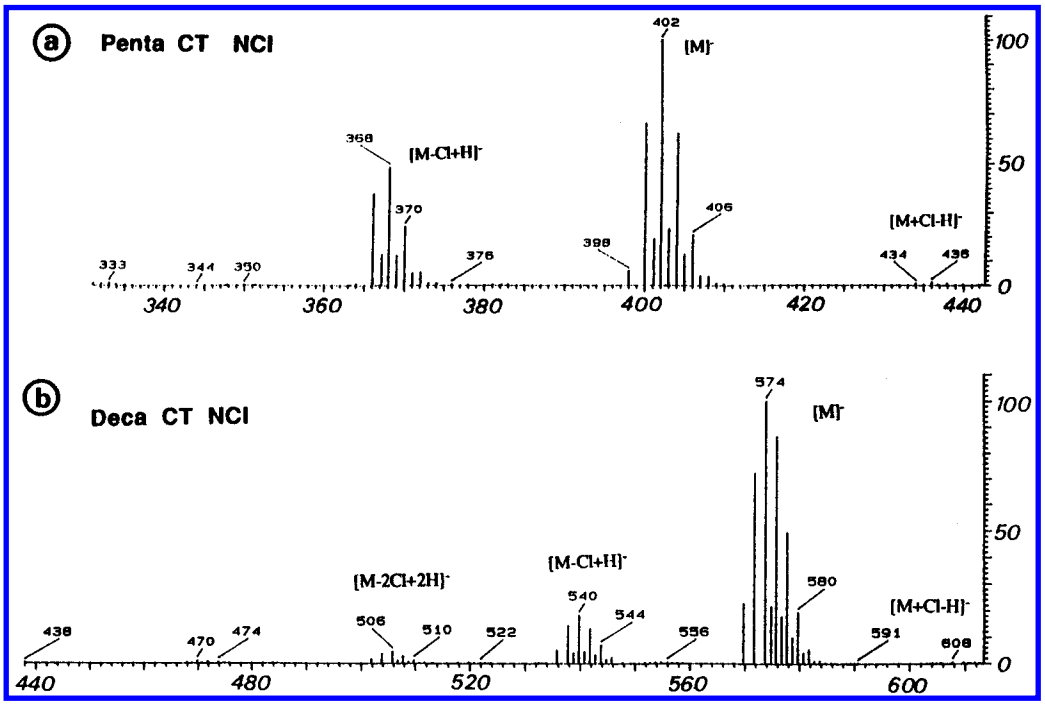

FIGURE 3. NCI mass spectra of (a) a penta-CT (NCI) and (b) a deca-CT (NCI). Some contamination of the spectra by a tetra-CT and a nona-CT, respectively, cannot be excluded.

homogenizing, an amount of tissue or sediment was ground with anhydrous sodium sulfate (sodium sulfate/water 3:1 w/w). Subsequently, the dry powder was transferred to a Sohxlet cartridge, which was stored overnight in a desiccator and, next, extracted for 12 h in a Sohxlet apparatus with 500 mL *n*-pentane/dichloromethane 1:1 (v/v). In order to remove the dichloromethane, the extracts were evaporated to ~10 mL on a rotary evaporator (water bath temperature 40 °C) after the addition of 10 mL of isooctane as a keeper and quantitatively transferred to 50 mL volumetric cylinders and made to volume with *n*-pentane. For the removal of lipids from biota extracts, and of organic material from sediment extracts, 25 mL of concentrated sulfuric acid was carefully added and the cylinders were covered with clock glasses to avoid contamination. The cylinders were occasionally carefully shaken. After 12−16 h, the clear *n*-pentane layers were transferred quantitatively to round-bottom flasks and evaporated on a rotary evaporator to ~20 mL. The extracts were cleaned over 15 g Al_2O_3·6% H_2O columns (2 cm i.d., elution with 60 mL of *n*-pentane) and 1.8 g SiO_2·1.5% H_2O columns [6 mm i.d., elution with 11 mL of diethyl ether/isooctane 5:95 (v/v)]. Subsequently 1 mL of 1,2,3,4-tetrachloronaphthalene (TCN) (8 ng/mL) was added as an internal standard, and the extracts were evaporated under a nitrogen stream to ~200 μL. Total lipid determinations were carried out according to the method of Bligh and Dyer (*17*, *18*), based on a chloroform/methanol extraction. GC/NCI-MS was carried out on a Hewlett-Packard 5988A GC/MS under the following conditions: column, WCOT CP Sil12 (58% CP-Sil8 + 42% CP-Sil19), 45 m, 0.25 mm i.d., film thickness 0.20 μm (gift of Dr. J. Buyten, Chrompack, Middelburg, The Netherlands); carrier gas, He, 100kPa; injection, splitless; temperature, 295 °C; splitter closing time, 2.5 min. GC oven program, 3 min at 90 °C, 30 °C/min to 210 °C, 3.5 °C/min to 280 °C, and 53 min at 280 °C; postrun, 20 min at 290 °C. Source temperature, 100 °C; ionization gas, methane; source pressure, 1 Torr; transfer line temperature, 290 °C. Scanned ions (*m*/*z*) 264, 266 (TCN), 332, 334 (trichloroterphenyl), 366, 368 (tetrachloroterphenyl), 400, 402 (pentachloroterphenyl), 436, 438 (hexachloroterphenyl), 470, 472 (heptachloroterphenyl), 504, 506 (octachloroterphenyl), 538, 540 (nonachloroterphenyl), 572, 574 (decachloroterphenyl), and 606, 608 (undecachloroterphenyl).

The PCTs were quantified by comparing the total area of all relevant peaks in the total ion chromatogram (TIC) of the samples with those of the A5442 or A5460 standards. These results were compared with quantification based on the measurement of all relevant peaks of one *m*/*z* ratio (single-ion chromatograms (SIC)). Results were corrected for recovery and expressed as micrograms per kilogram of wet weight or micrograms per kilogram of lipid weight.

Results and Discussion

Use of GC/NCI-MS. In the present study NCI was preferred to EI as the MS ionization method because of its higher sensitivity and selectivity for the analytes of interest. Only lower chlorinated terphenyls (CTs) (≤4 chlorine atoms) showed a lower sensitivity with NCI. Lower chlorinated terphenyls are, however, hardly present in A5442 and even less so in A5460. Hale et al. (*10*) reported the presence of lower CTs in sediments and shellfish from the Chesapeake Bay, due to a discharge of A5432. Monsanto has, however, produced substantially more A5460 than A5432 (*9*). NCI mass spectra of a penta- and a deca-CT are shown in Figure 3.

Other polychlorinated compounds like PCBs, polychlorinated naphthalenes (PCNs), and some organochlorine pesticides can cause false positive PCT signals. In capillary GC, most of these compounds elute in front of the PCTs (Figure 4). Only higher PCBs overlap with lower chlorinated PCTs (≤5 chlorine atoms). A preseparation of PCTs from PCBs would completely solve this problem. However, the only preseparation of PCTs and PCBs reported until now, based on gel permeation chromatography (*19*), does not provide a complete separation. Because tetra- and lower CTs and octa−deca-CBs were only of minor importance in

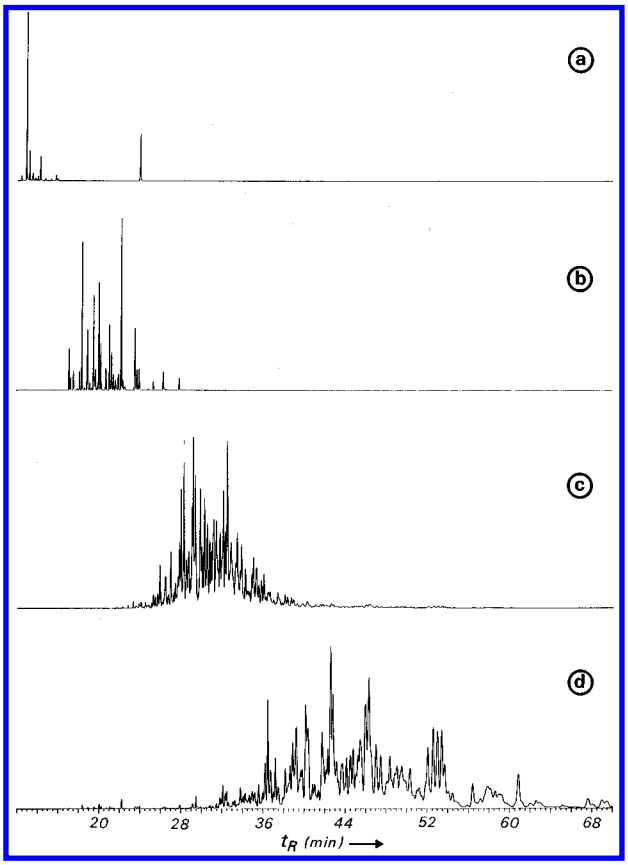

FIGURE 4. Total ion chromatograms (NCI) of technical mixtures of (a) polychlorinated naphthalenes (Halowax, HW 1014), (b) PCBs (A1260), (c) PCTs, (A5442), and (d) PCTs (A5460); CP Sil 12 column, 45 m × 0.20 mm × 0.20 μm.

the samples analyzed in this study, no corrections for possibly coeluting higher chlorinated PCBs were made.

Comparison with Other Detection Methods. To our knowledge GC/NCI-MS has been used for the quantification of PCTs only once, viz. by Canton and Grimalt (*20*). They used GC/NCI-MS for a qualitative study of the composition of PCT mixtures in sediments but did not report detailed information on analyte (mixture) detectability and repeatability. Besides, they used 0.32 mm i.d. capillary columns, which detracts from the resolution that can be obtained. The paper of de Kok et al. (*7*) shows the state of the art of PCT determination in the early 1980s. The authors then recommended capillary GC/ECD as the most appropriate method for the determination of PCTs. Compared with that method, GC/NCI-MS offers a much better selectivity and sensitivity. Today, for compounds with four or more chlorine atoms detection limits obtained with NCI-MS are 10-fold better than those obtained with ECD. Besides, GC/NCI-MS provides information on the number of chlorine atoms of the different CT congeners, so that the chlorination degree of PCTs in samples can be estimated.

In a recent study, Hale et al. (*10*) used GC/electrolytic conductivity detection (ELCD) to determine PCTs and reported detection limits of ~10 μg/kg of dry weight in sediment and 3 μg/kg of wet weight in shellfish, expressed as A5460. The detection limit of our GC/NCI-MS method is ~0.1 μg/kg of wet weight in sediment and biota, expressed as A5442. When A5460 is used as a standard, this detection limit would even be 5-fold lower, because of the stronger response of higher chlorinated CTs. The selectivity of the GC/ELCD method of Hale et al. (*10*) is similar to that of GC/ECD rather than GC/NCI-MS. The repeatability of our method had a relative standard deviation of 15% for the 5-fold analysis of an eel sample (total PCT concentration expressed as A5442, 52−73 μg/kg). PCT recoveries calculated from standards that were subjected to the total analytical procedure, ranged from 88 to 101% for all samples analyzed.

Errors in Calculation. Even with high-resolution capillary GC columns, a complete separation of PCT congeners is not possible. The calculation of PCT concentrations is therefore based on pattern comparison and can be influenced by the method used. In order to assess which differences are caused by the use of different ions and different calculation methods, an experiment was carried out in which the PCT concentrations in four biota and one sediment sample were determined by seven different methods: TIC using A5442 or A5460 as a standard, SIC using m/z 436 (hexa-CT) and A5442 as a standard, SIC using m/z 470 (hepta-CT) and A5442 or A5460 as a standard, and SIC using m/z 506 (octa-CT) and A5442 or A5460 as a standard. Table 3 shows that replacing A5442 as a standard by A5460 in the TIC method causes a 30% difference in the results found for the biota samples, and an about 5-fold difference for the sediment sample. The differences in the experimentally calculated concentrations are even larger when SIC is used. The data of Table 3 show that, for biota, with m/z 470 a constant value of ~5 is found for the A5442/A5460 ratio; for m/z 506 this value is, however, ~50! This is due to the different concentrations of hexa- and hepta-CTs in A5442 and A5460. These results show that especially the use of only one ion easily leads to ambiguous results. The results are a clear plea for the TIC approach. For this reason we have scanned 18 ions (see GC/MS conditions) for the analyses of the samples reported in Table 5. Additionally, proper selection of the standard is important in GC/NCI-MS, especially because of the large differences in response factors observed with this technique, larger errors will be made than with techniques such as GC/ECD or GC/EI-MS. No information on the response factors of individual CTs is available in the literature. As an alternative, Figure 5 shows relative response factors of six CBs with a different number of chlorine atoms for GC/ECD, GC/EI-MS, GC/NCI-MS (SIC), and GC/NCI-MS (TIC). The highly different NCI signals of CBs with less than five chlorine atoms and higher CBs are obvious. This suggests that, in case of PCT determination on the basis of Aroclor equivalents, the selection of a technical mixture will be rather critical. As an example, Table 4 shows the results of an experiment in which the percentages of hexa-, hepta-, and octa-CTs in A5442, A5460, and a 1:1 mixture of these Aroclors were determined by GC/NCI-MS (TIC). The ions m/z 436 and 438 (hexa-CT), 470 and 472 (hepta-CT), and 504 and 506 (octa-CT) were scanned in A5442, A5460, and the 1:1 mixture. With lack of individual congeners the accuracy problems are similar to those described above for environmental samples. The large differences between the experimental results for the A5442/A5460 mixture and the values calculated on the basis of the assumption of equal response factors for all CBs clearly show that errors of, typically, 30−40% can be expected if the calculations are not carried out on the basis of individual CT congeners. If the standard selected contains a higher percentage of lower (or higher) CTs than the sample, the experimentally calculated result will be lower (or higher) than the real value.

TABLE 3

PCT Concentrations (μg/kg of Wet Weight) Corrected for Recovery and Calculated by Different Methods

	TIC		SIC				
				m/z 470		*m/z* 506	
	A5442	A5460	*m/z* 436 A5442	A5442	A5460	A5442	A5460
correlation coefficient calibration curve	0.9998	0.9998	0.9998	0.9998	0.9999	0.9996	0.9998
recovery (%)	94	91	93	93	89	89	88
cod liver, southern North sea 1992	410	300	490	2200	440	1300	26
tufted duck egg, Zoommeer 1991	35	25	32	140	26	110	20
whitebeaked dolphin, North Sea 1990	7400	5500	9600	42000	8600	19000	370
eel fillet, Rhine Lobith 1992	200	150	250	1300	260	1100	23
sediment, Waal Tiel 1992	100	17	46	710	74	1400	33

TABLE 4

Percentages of Hexa-, Hepta-, and Octa-CTs in Aroclor Mixtures

mixture	hexa-CTs (%)	hepta-CTs (%)	octa-CTs (%)
A5442	29	4.1	1.6
A5460	3.8	11	32
A5442/A5460 (1:1)	11	9.3	24

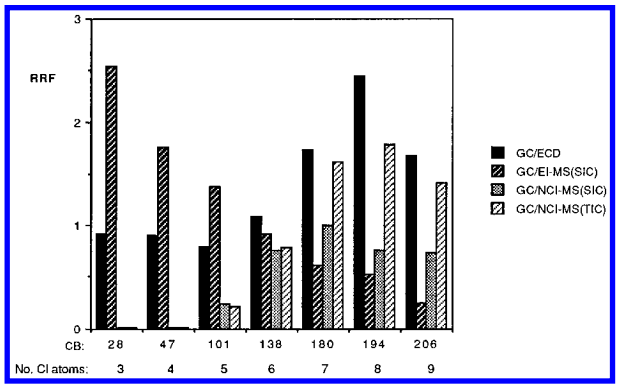

FIGURE 5. Response factors relative to CB 153 (RRF) of CBs with a different number of chlorine atoms for GC/ECD, GC/EI-MS, GC/NCI-MS (SIC), and GC/NCI-MS (TIC).

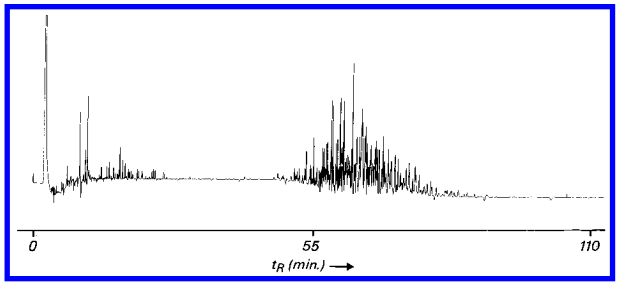

FIGURE 6. GC/ECD chromatogram of Aroclor 5442: CP Sil 8 column, 50 m × 0.15 mm × 0.30 μm; Temperature program, 3 min at 90 °C, 30 °C/min to 215 °C, 30 min at 215 °C, and 5 °C/min to 280 °C.

Different Sources of Aroclor Mixtures. The peak pattern which we observed when analyzing A5442 either by GC/NCI-MS or by GC/ECD (Figure 6) is completely different from that reported by de Kok et al. (*7*). We find only one group of peaks in our chromatograms, whereas de Kok et al. found two groups. They consequently suggested that A5442 very likely is a mixture of A5432 and A5460. Both the A5442 mixture of de Kok et al. and our A5442 mixture originate from Monsanto, but that of de Kok et al. was produced in the United States whereas our A5442 mixture was produced in the UK. De Kok et al. already reported that other authors had also found patterns deviating from theirs. Analysis of more batches of Aroclor is required to confirm if indeed several types of A5442, and maybe also of other Aroclor mixtures, are present on the market. If so, another source of error should be taken into account when pattern recognition is used for the determination of PCTs.

PCT Concentrations in Biota and Sediments. Total PCT concentrations were determined in a number of biota and sediment samples. A5442 was selected as the reference because its pattern best resembled that of most samples (cf. Figure 7); TIC was used to reduce possible errors as much as possible. The results are given in Table 5. These percentages were calculated by using the data on A5442 of Table 4 as a reference. The results (which, for obvious reasons, should be considered as semiquantitative estimates rather than precise calculations) indicate that hexa- and hepta-CTs represent 50−70% of the total PCT concentration in biota and 40−60% of that in sediment.

Figure 7 shows ion profiles of *m/z* 436 (hexa-CT) and 470 (hepta-CT) in A5442 and eel and sediment from the Nieuwe Merwede. In biota hexa-CTs are the major group of congeners whereas in sediment the hepta-CTs dominate. Tetra-, penta-, nona-, deca-, and traces of undeca-CTs were also detected in the sediment samples, but in considerable lower concentrations than the hexa−octa-CTs.

Correlation of PCT and PCB Concentrations. The total PCB concentrations in biota and sediment samples are included in Table 5. They were calculated from the sum of 30 CB congeners, which may be supposed to represent ~65% of the total PCB concentration in environmental samples (*21*). There is a clear correlation between the total PCT and the total PCB concentrations (for biota $r = 0.926$, $n = 25$; for sediment, $r = 0.815$, $n = 5$). Figure 8 shows the correlation between total PCT and PCB concentrations in biota on a lipid weight basis. Figure 8 shows that PCTs are as widely distributed in the environment as PCBs. Total PCT concentrations in biota expressed as A5442 equivalents are in general 1−10% of the total PCB concentration, with a mean of 4% ($n = 25$). These percentages are higher than those reported by Renberg and Sundström (*22*), who found PCT levels of 0.3−1.6% of the PCB levels in white-tailed eagles and grey seals from Sweden. The wide distribution of PCTs was not recognized by Zitko et al. (*23*), although it is understandable that in those years not enough sensitivity could be obtained. Actually, the ratio in biota roughly reflects the production volumes of PCBs and PCTs. Higher PCT/PCB ratios were found in the five sediment samples analyzed: 10−24% with a mean of 16% ($n = 5$). A possible explanation for the high PCT/PCB ratios is a better adsorption of PCTs than PCBs to sediments. From four of the five sediment sampling sites eel fillets were also

TABLE 5

PCT Concentrations in Biota and Sediments, Based on TIC Using A5442 as a Standard, and Corresponding PCB Concentrations

Sample	Latin name	total PCT (TIC) (mg/kg of wet wt)	% fat or % org C	concn (mg/kg of lipid wt)			
				total PCT (TIC)	PCB-153	total PCB	total PCT/total PCB (%)
eel fillet, Rhine Lobith 1992	*Anguilla anguilla*	0.20	11.7	1.8	4.4	42	4.3
eel fillet, Roer Vlodrop 1992	*A. anguilla*	0.10	19.2	0.52	1.7	21	2.5
eel fillet, Meuse Eijsden 1992	*A. anguilla*	0.06	14	0.40	1.5	26	1.5
eel fillet, Haringvliet East 1992	*A. anguilla*	0.14	11.8	1.2	8.1	45	2.7
eel fillet, Yssel Lake 1992	*A. anguilla*	0.05	26	0.20	0.50	3.5	5.7
eel fillet, Meuse Keizersveer 1991	*A. anguilla*	0.13	14.1	0.91	4.0	27	3.4
eel fillet, Nieuwe Merwede 1992	*A. anguilla*	0.16	17.2	0.92	4.3	39	2.4
eel fillet, Lauwersmeer 1992	*A. anguilla*	0.006	13.8	0.04	0.14	1.3	3.3
eel fillet, Hollands Diep 1992	*A. anguilla*	0.18	15.1	1.2	4.0	26	4.6
eel fillet, Ketelmeer 1992	*A. anguilla*	0.09	19.2	0.44	1.3	9.8	4.5
eel fillet, Westerschelde 1992	*A. anguilla*	0.01	11.4	0.12	1.6	14	0.86
pike perch fillet, Hollandse Yssel 1990	*Stizostedion lucioperca*	0.005	0.89	0.53	2.5	31	1.7
cod liver, southern North Sea 1992	*Gadus morhua*	0.41	51.2	0.81	2.1	11	7.4
cod liver, northern North Sea 1992	*G. morhua*	0.04	52	0.08	0.09	0.84	9.9
twaite shad fillet, southern North Sea 1991	*Alosa fallax*	0.01	7.8	0.17	0.95	7.5	2.3
plaice fillet, Doggersbank 1990	*Pleuronectus platessa*	0.001	1.0	0.11	0.09	0.93	12
herring fillet, Dutch coast 1991	*Clupea harengus*	0.003	17.2	0.02	0.08	0.77	2.1
whitebeaked dolphin blubber, North Sea 1991	*Lagenorynchus albirostris*	7.4	69.6	11	48	240	4.6
whitebeaked dolphin liver, North Sea 1991	*L. albirostris*	0.38	5.3	7.1	45	310	2.3
harbor porpoise blubber, North Sea 1990	*Phoceana phoceana*	1.9	80.6	2.3	19	88	2.6
gentoo penguin muscle, Falklands 1991	*Phygoscelis papua*	0.0003	1.75	0.02	na[b]	na	
gentoo penguin liver, Falklands 1991	*P. papua*	0.002	5.3	0.03	0.04	0.47	5.7
sheldrake egg, Prinsesseplaat 1991	*Tadorna tadorna*	0.06	18.2	0.31	6.2	42	0.74
tufted duck egg, Zoommeer 1991	*Aythya fuligula*	0.04	17.3	0.20	0.58	6.6	3.0
cormorant liver, Ketelmeer 1990	*Phalacrocorax carbo*	0.12	4.0	3.0	15	93	3.2
cormorant liver, Ketelmeer 1990	*P. carbo*	0.09	3.4	2.7	14	75	3.6
sediment,[a] Haringvliet East 1992 (dw 61%)		0.02	1.62	1.4	0.93	13	10
sediment,[a] Rhine Lobith 1992 (dw 65%)		0.08	2.95	2.8	1.3	19	15
sediment,[a] Meuse Keizersveer 1992 (dw 64%)		0.06	2.73	2.0	0.98	14	15
sediment,[a] Nieuwe Merwede 1992 (dw 63%)		0.09	1.89	4.5	1.2	20	24
sediment,[a] Waal Tiel 1992 (dw 66%)		0.10	2.33	4.3	1.8	31	14

[a] Total PCT, PCB 153, and total PCB (calculated from 30 CB congeners as 65% of the total PCB concentration) concentrations in sediment, expressed in micrograms per kilogram total organic carbon. [b] na, not analyzed.

analyzed (Table 5). The fish/sediment ratio for PCTs (expressed as μg/kg of lipid weight in fish relative to μg/kg total organic carbon in sediment) ranges from 0.2 to 1, whereas for PCBs this ratio ranges from 2 to 4. This confirms the higher adsorption of PCTs to sediments.

Comparison with Literature Data. Literature data on PCTs must be treated with care because of the large variation in analytical procedures and calculation methods used. Because of the lack of quality control data on PCTs and considering the well-known poor intercomparability of total PCB determinations in the 1970s, literature data on PCTs probably show at best only the order of magnitude of the PCT contamination present. Actually, the PCT concentrations in eel from the Yssel Lake found in this study (Table 5) are rather similar to PCT concentrations in eel from the same location, reported by Freudenthal and Greve (*24*) some 20 years ago (1973) (Table 2). PCT concentrations in eel from the estuaries of the rivers Rhine and Meuse (1992) are higher (Table 5); this is similar to the situation encountered with PCBs. PCT concentrations in the marine mammals analyzed are higher than PCT concentrations in Swedish grey seal (*22*). PCT concentrations in herring eggs and herring fat from the Bay of Fundy, Canada (*23*) (Table 2) are higher than PCT concentrations in most North Sea fish (Table 5), except southern North Sea cod liver. The absence of PCTs in cormorant livers from the Bay of Fundy (Table 2) reported by Zitko et al. (*23*) was presumbably due to a lack of sensitivity. Whereas we could easily detect ~100 μg/kg of wet weight of PCTs in cormorant livers from the Ketelmeer, the GC/ECD chromatograms in the quoted paper indicate that this must have been their detection limit.

This is the first report on the presence of PCTs in sub-Antarctic organisms. Although the PCT levels are relatively low, the PCT/PCB ratio agrees with PCT/PCB ratios in organisms from other locations. An increasing PCB contamination of this area was suggested (*25*). The PCT/PCB ratios found may suggest that PCTs follow the same trend.

The PCT concentrations in five sediment samples from Dutch rivers (Table 5) are of the same order of magnitude as the PCT concentrations in sediments from the Spanish Atlantic coast (Table 2). Extremely high PCT concentrations have been reported by Hale et al. (*10*, *19*) in sediments of the James river and Chesapeake Bay in the United States (Table 2). The PCT patterns of those samples were closely similar to those of A5432, with penta-CTs being the main constituents. Contamination was probably caused by recent, local discharges of PCTs, because PCTs were only found in the upper layer of the sediments.

Conclusions

During the performance of trace-level determinations of PCTs, similar problems are encountered as when analyzing other complex mixtures of halogenated hydrocarbons. There are a high number of congeners, which cannot be separated by single-column high-resolution GC, a lack of commercially available congeners, and a lack of other procedures for a proper determination of the total con-

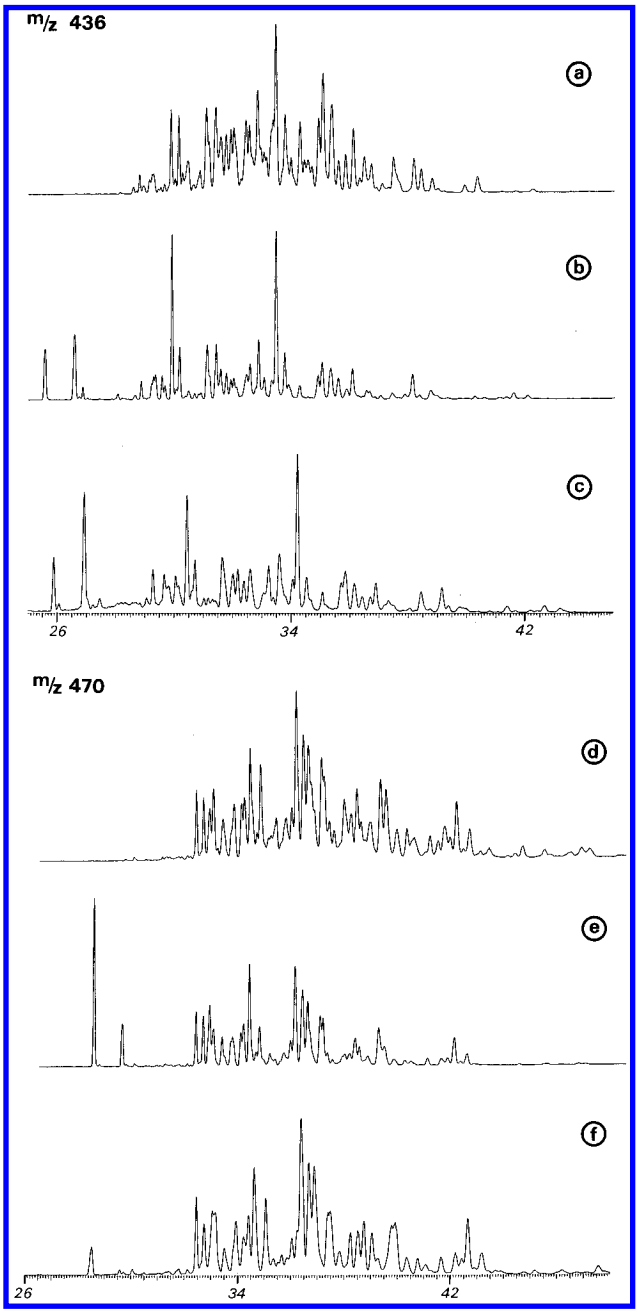

FIGURE 7. Single-ion chromatograms of (a) Aroclor 5442 (*m/z* 436); (b) eel, Nieuwe Merwede (*m/z* 436); (c) sediment, Nieuwe Merwede (*m/z* 436); (d) Aroclor 5442 (*m/z* 470); (e) eel, Nieuwe Merwede (*m/z* 470); and (f) sediment, Nieuwe Merwede (*m/z* 470). CP Sil 12 column, 45 m × 0.20 mm × 0.20 μm.

centration. Compared with PCBs, which have been studied extensively and are now determined routinely using a congener-specific approach, PCTs present a more daunting problem because of the 40-fold larger number of congeners and because of the absence of commercially available higher CTs. This makes pattern comparison the best analytical approach today.

The use of GC/NCI-MS, which provides much better selectivity and higher sensitivity than GC/ECD, enables a more reliable determination of PCTs. The peak patterns of the Aroclor mixture used as a standard and those of the samples should resemble each other as much as possible to avoid significant errors in the results, which under unfavorable conditions can be as high as 500%. In the present study, A5442 showed the best resemblance to the

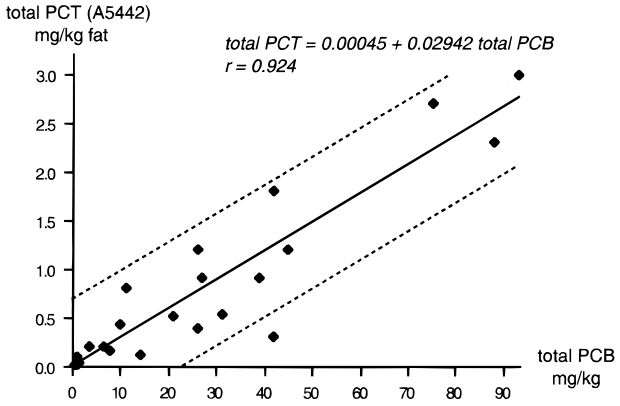

FIGURE 8. Correlation between total PCT and total PCB concentrations on a lipid weight basis in biota. Dotted lines show 95% confidence interval.

PCT patterns of biota and sediment samples analyzed. The type and source of the standard mixture used should be reported in each study.

In the present study, the percentage of hexa- + hepta-CTs was calculated to be 50−70% in biota and 40−60% in sediment samples, with hexa-CTs as the major group of CT congeners present in biota and hepta-CTs as the dominant group in sediments.

The present study shows a distinct correlation between total PCT and total PCB concentrations in the environmental samples studied, which suggests that PCTs have an environmental distribution similar to the PCBs. In five sediment samples from Dutch rivers, total PCT concentrations were 10−24% of the total PCB concentrations. PCT concentrations in aquatic biota were 1−10% (mean, 4%) of the PCB concentrations in the same samples. The mean PCT/PCB ratio in aquatic biota roughly corresponds with the ratio of the production figures of PCBs and PCTs. The relatively high PCT concentrations in the sediment samples analyzed probably reflect a relatively stronger adsorption of PCTs.

The reported environmental levels of PCTs, which are rather unexpectedly high, should stimulate more extensive research on the environmental distribution of this compound class and the possible ecological implications and risks for human health. The present GC/NCI-MS procedure is sufficiently sensitive and selective to obtain semiquantitative data on the PCT contamination level of environmental samples.

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