Congener specific analysis of polychlorinated terphenyls

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ABSTRACT

In order to identify and to quantify polychlorinated terphenyls (PCT) in environmental matrices, the chromatographic behavior of coplanar and non-coplanar congeners was evaluated. A mixture of 16 single PCT congeners was used for method development. Four of these compounds were synthesized for the first time by SUZUKI-coupling reaction. These were p-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″,5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and m-PCT (2,2″,3,3″,5,5″-hexachloro-). They were characterized by NMR (^{1}H, ^{13}C) spectroscopy. By means of the new column chromatographic clean-up reported here, a good matrix removal and the separation of the coplanar PCT congeners from the non-coplanar ones was obtained. The recovery rates for all congeners were good for the PCT in different test matrices like fat, charcoal, and soil. The quality of the clean-up, the separation and the recovery rates were determined by GC/MS analysis. The method was applied for the first time to a real sample from a fire accident, where different PCT, obviously formed during the combustion process, were found. The conclusion is drawn that this method is suitable for the analysis of PCT in different environmental samples.

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1. Introduction

In the past, about 60 000 tons of PCT were produced worldwide. The application patterns of PCT were similar to those of PCB due to similar chemical and physical properties of both substance groups (Birn and Jung, 1993; de Boer, 2000). From the former application fields, disposal sites like landfills as well as from combustion processes (new formation) PCT are emitted into the environment as low volatile, persistent, and bioaccumulating substances. In spite of comparably limited knowledge about this substance group, its environmental and toxicological relevance should not be neglected. The main reason for this lack of knowledge is that the 8557 possible PCT congeners (Remberg et al., 1998) could not be handled sufficiently by common gas chromatographic techniques so far. Furthermore, with a few exceptions, single reference substances are not available, which are necessary for the development of suitable analytical methods. In consequence, published data on the occurrence of PCT should be dealt with utmost care, due to strongly varying analytical procedures and calculation methods used (Gallagher et al., 1993; Wester et al., 1996; Fernandez et al., 1998).
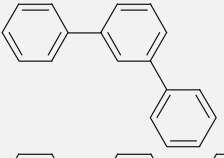
Some approaches were undertaken in the past in order to synthesize particular PCT congeners as authentic standards for analytical investigations. First works in this area were done by Chittim et al. (1977), they synthesized 22 PCT congeners. At the beginning of the new millennium the next approach in the synthesis of PCT was successfully started (Bahadir et al., 2003; Hopf et al., 2007). The syntheses are based on the SUZUKI-coupling (Miyaura et al., 1981; Lehmler and Robertson, 2001). Within the work, introduced here, the number of single PCT congeners was extended. Four new congeners were synthesized: p-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″,5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and m-PCT (2,2″,3,3″,5,5″-hexachloro-). These compounds were characterized by NMR (^{1}H, ^{13}C). In addition, the NMR data of earlier synthesized congeners are introduced, as well (s. Appendix A). As a result, 38 single congeners with different degrees of chlorination (1–6 and 14) are now available, including coplanar and non-coplanar species. Most of all PCT are of non-coplanar structure. These are all compounds with at least one substitute (a chlorine atom or a phenyl-ring) in ortho-position. The amount of compounds with no such ortho-substitution is quite low, only 61 congeners as shown in Table 1 (Remberg et al., 1998).

As already mentioned, no standardized and generally accepted method for PCT quantification is known, yet. As can be seen from Table 1, there are 20 para- and 41 meta-terphenyls among the 8557 congeners with no ortho chlorine atom. This substitution pattern easily allows molecular planarity. On the one hand, derived from PCB, PCDD and PCDF, those congeners are suspected of being most toxic among the PCT. On the other hand, this special property of planarity can be used to separate these interesting PCT congeners by an additional column chromatographic step integrated into a regular clean-up procedure. Thus, gas chromatographic separation of the selected PCT now becomes possible and some of those

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Table 1
Number of all non-ortho substituted terphenyls.

Basic structure of terphenyl congeners (meta, para)	Degree of chlorination							Sum of species
	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	
	3	7	10	10	7	3	1	41
	2	5	5	5	2	1	–	20

planar congeners can be chosen and analyzed as indicator substances with GC/MS, following the well established strategy of e.g. PCDD/PCDF-, PCB-, or PAH-analyses. Besides the synthesis of reference standards, the development and a first application of this procedure is described in the following.

2. Materials and methods

2,6-Dichlorobromobenzene, 1,3-dibromobenzene, benzene-1,4-diboronic acid, 2,3,5-trichlorobenzeneboronic acid, 3,4-dichlorobenzeneboronic acid, 3,5-dichlorobenzeneboronic acid and tetrakis-(triphenylphosphine)palladium(0) were commercially available with a purity of 97–98% (Lancaster Synthesis GmbH, Acros Organics). 1,4-Dibromo-2,5-dichlorobenzene was synthesized by Sandmeyer reaction. Solvents were purchased in p.a. quality (Merck AG). The sorbents Alumina B-Super I and silicagel (63–200 mesh) were purchased from ICN Biomedicals GmbH, and florisil for residue analysis (0.150–0.250 mm) was purchased from Merck AG.

The congeners PCT 1, 8 and 16 (numbering according to Table 2) were purchased from Promochem GmbH, PCT 2, 3, 5, 6 and 7 were synthesized in the Institute of Organic Chemistry, TU Braunschweig, PCT 9, 10, 13 and 15 were synthesized earlier in the own institute (Bahadir et al., 2003; Hopf et al., 2007).

Four new PCT congeners were synthesized according to the SUZUKI-coupling: p-PCT (2,2″,6,6″-tetrachloro-, 2′,3,3″,4,4″, 5′,-hexachloro-, 2′,3,3″,5,5′,5″-hexachloro-) and m-PCT (2,2″,3,3″,5, 5″-hexachloro-). The 2,2″,6,6″-tetrachloro-p-terphenyl was synthesized by reaction of one equivalent benzenediboronic acid with two equivalents bromobenzene, the other terphenyls were synthesized by the reaction of one equivalent dibromobenzene with two equivalents of benzenemonoboronic acid. The recrystallized terphenyls were characterized by NMR (^{1}H and ^{13}C) and GC/MS analysis.

NMR-spectra were obtained using a Bruker AM 400 at 400.1 MHz (^{1}H) and at 100.6 MHz (^{13}C), applying CDCl$_3$ as solvent and TMS as internal standard.

GC/MS analyses for PCT quantification were performed with an Agilent GC 6890 Series/Agilent MSD 5975C equipped with a DB5-MS column, 30 × 0.25 mm, film thickness 0.25 μm, single ion mode. Temperature program: 90 °C (2 min) – 17 °C min^{-1} to 200 °C – 3.5 °C min^{-1} to 300 °C (26 min). The following masses (m/z) were used for SIM-measurements of the PCT: monochloro: 264.0/266.0; dichloro: 298.0/300.0; trichloro: 332.0/334.0; tetrachloro: 365.9/367.9/369.9; pentachloro: 399.9/401.9/403.9; hexachloro: 433.9/435.9/437.9; tetradecachloro: 709.7/711.7/713.7. As internal standard for quality control, 1,2,3,4-tetrachlorodibenzo-p-dioxin was used.

For the clean-up procedure in general, column chromatography was conducted with self-prepared glass columns with 30 cm length and 1.6 cm inner diameter. The clean-up consists of four steps including alumina column, mixed silicagel column, again alumina column and florisil column.

The alumina columns were filled in with 30 g aluminium oxide (basic, activity I, 0% water), 10 g Na$_2$SO$_4$ and conditioned with 80 mL hexane. Three fractions were gained from elution with 80 mL hexane, 150 mL hexane/dichloromethane (99:1), and 250 mL hexane/dichloromethane (1:1).

The mixed silicagel column was filled in with 2 g silicagel neutral, 5 g silicagel 33% 1 M NaOH, 2 g silicagel neutral, 10 g silicagel 44% conc. H$_2$SO$_4$, 2 g silicagel neutral, and 10 g Na$_2$SO$_4$ on top. It was conditioned with 80 mL hexane. The elution was done with 250 mL hexane/dichloromethane (99:1).

The florisil column contained 23 g florisil (conditioning: 2 h at 180 °C, deactivation with 2% water) and 10 g Na$_2$SO$_4$. It was rinsed with 80 mL cyclohexane/dichloromethane (99:1) before use. The elution was done with 500 mL cyclohexane/dichloromethane (99:1) and with 250 mL dichloromethane. Both fractions were reduced to 1 mL and analyzed by GC/MS as described before.

For the sample preparation the matrix materials (1 g vegetable oil, 10 g homogenized dry soil (type: Cambisol) and 5 g fine powdered wood charcoal) were spiked with 100 μL of PCT standard solution with a concentration of 20 μg mL^{-1} for each of the 16 PCT as listed in Table 2.

The spiked oil sample was shaken for 2 min, diluted with 2 mL hexane and directly introduced to the column. Na$_2$SO$_4$ (3 and 1 g) was added to the spiked soil and charcoal samples, before they were extracted with 80 mL toluene in a soxhlet extractor for 16 h. The volume of the extracts was reduced to approximately 2 mL before column chromatography.

3. Results and discussion

For the development of the clean-up procedure a mixture of 16 PCT with different chlorination degrees, mono- to hexa as well as tetradecachlorinated congeners, was used. This mixture contained four coplanar and 12 non-coplanar PCT (Table 2).

The clean-up procedure for PCT, as introduced here, is based on the classical method for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans, using alumina columns and a mixed silicagel column (Dettmer et al., 1998). The first approach in this work was the optimization of that column chromatography (absorbents, solvents) for PCT analysis. The second, more important step was the introduction of an additional florisil column. This one is responsible for the separation of the PCT mixture into coplanar and non-planar constituents. The idea goes back to Ebert et al. (1999), who successfully separated non-planar polybrominated diphenylethers from planar polybrominated dibenzo-p-dioxins and dibenzofurans with florisil adsorbent.

In the first step of the clean-up, basic alumina was used for removing lipids and other fatty compounds of the matrix. Also

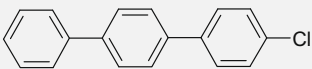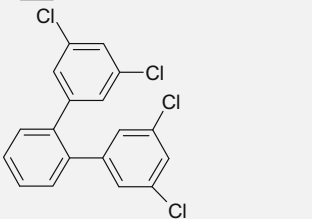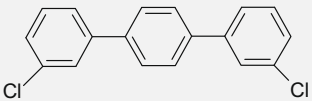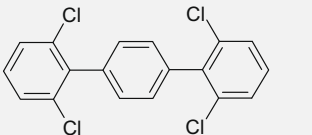**Table 2**
List of compounds for PCT analysis.
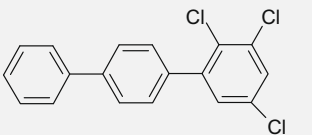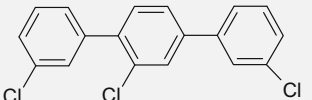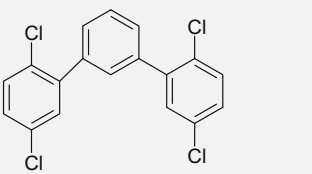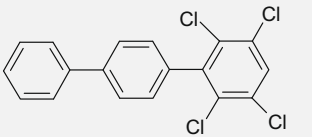
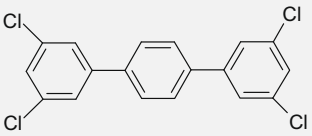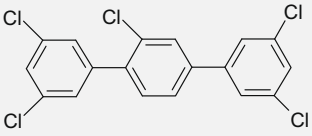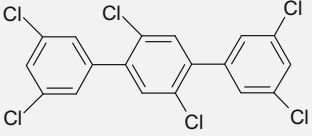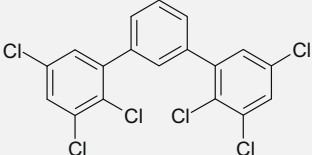| Abbreviation	Substance	Structural formula	GC/MS retention time (min)
PCT 1[*]	4-Monochloro-p-terphenyl		19.38
PCT 2	3,3″,5,5″-Tetrachloro-o-terphenyl		20.58
PCT 3[*]	3,3″-Dichloro-p-terphenyl		23.23
PCT 4	2,2″,6,6″-Tetrachloro-p-terphenyl		23.65
PCT 5	2,3,5-Trichloro-p-terphenyl		24.26
PCT 6	2′,3,3″-Trichloro-p-terphenyl		24.94
PCT 7	2,2″,5,5″-Tetrachloro-m-terphenyl		25.14
PCT 8	2,3,5,6-Tetrachloro-p-terphenyl		26.49
PCT 9[*]	3,3″,5,5″-Tetrachloro-p-terphenyl		29.75
PCT 10	2′,3,3″,5,5″-Pentachloro-p-terphenyl		30.99
PCT 11	2′,3,3″,5,5′,5″-Hexachloro-p-terphenyl		31.64
PCT 12	2,2″,3,3″,5,5″-Hexachloro-m-terphenyl		32.04

Table 2 (continued)

Abbreviation	Substance	Structural formula	GC/MS retention time (min)
PCT 13	2,2″,3,3″,5,5″-Hexachloro-p-terphenyl		33.33
PCT 14	2′,3,3″,4,4″,5′-Hexachloro-p-terphenyl		34.39
PCT 15[*]	3,3″,4,4″,5,5″-Hexachloro-p-terphenyl		39.44
PCT 16	Tetradecachloro-m-terphenyl		58.51

[*] Coplanar PCT congener.

other non-polar or semipolar compounds like PAH and PCB were separated. The recovery of all PCT congeners in the third fraction (hexane/dichloromethane 99:1) ranged from 91% to 137%. The second column with mixed silicagel was applicable for removing lipids, oxidable and basic compounds (Ebert et al., 1999). The recovery rates of the PCT were between 92% and 118%. The third column with alumina provided the same properties as the first one. It was also included for removing reaction products, probably eluted from column two.

In order to adjust the florisil column to its purpose, the properties of solvents and solvent mixtures with different polarities as well as different amounts of the florisil adsorbent and its activity (0%, 1% and 2% deactivation with water) were tested. Finally, the best separation results were obtained with the combination of 23 g florisil, deactivated with 2% water, with a fractional elution applying 500 mL of a cyclohexane/dichloromethane-mixture (99:1) and pure dichloromethane (250 mL), respectively.

The separation of non-coplanar from coplanar PCT congeners, first tested without matrix, was good. The non-coplanar compounds were collected in fraction 1 and three coplanar terphenyls (PCT 3, PCT 9 and PCT 15) were almost completely collected in fraction 2. Only PCT 1 was lost in the course of the clean-up procedure due to its higher solubility in organic solvents. This, however, was considered as being less important. It can be assumed that the monochloro-terphenyls are of minor toxicity, considering the related data on PCDD/F and PCB.

In the following, test matrices were choosen which represent typical environmental samples. These were fat (vegetable oil), resembling matrices from animals or humans, charcoal resembling residues from combustion processes, and soil, also representing sediment. The clean-up and separation procedures were practically tested with the impurities in the matrices involved.

3.1. PCT analysis in fat

The enrichment of halogenated POPs in fatty matrix is well known and also PCT were detected in fatty samples from the bio-sphere, in the past (Jensen and Jorgensen, 1983). Due to the solubilities, PCT could not be extracted from this matrix by means of soxhlet extraction. The spiked and diluted fatty matrix was added directly to the first column. One gram of fat was applied in order to prevent an overload of the column with organic substances. The recovery rates of PCT separated from fatty matrix with the aid of the four column clean-up procedure are shown in Fig. 1.

As can be seen from the Fig. 1, the recovery rates of the coplanar PCT 3, 9 and 15 of the fraction 2 from florisil column were quite good. These compounds could be completely separated from non-coplanar PCT, which were collected in fraction 1. The elution of the PCT into fraction 1 was low, but, as discussed in Section 1, it was not intended to consider the non-coplanar congeners in the course of analysis. PCT 1 was not detected after florisil column.
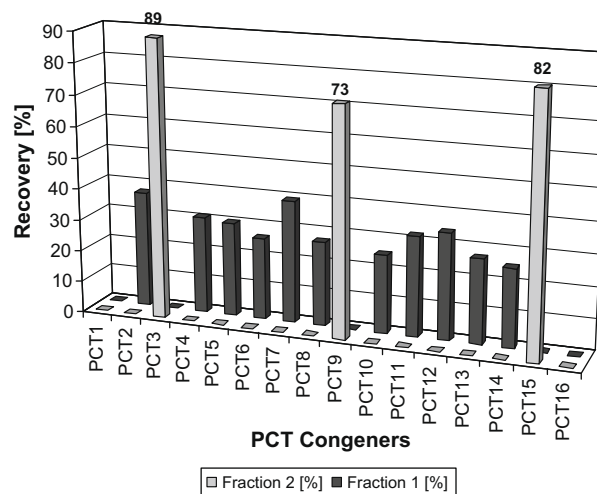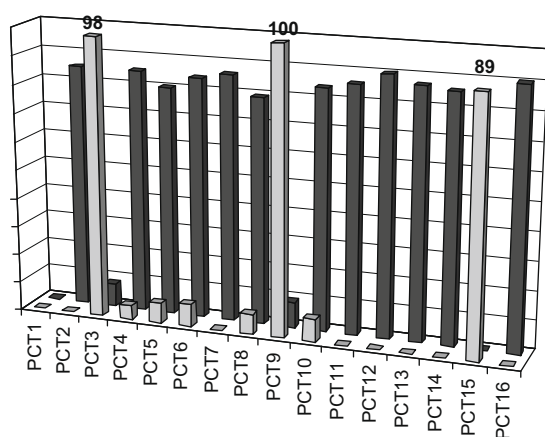

Fig. 1. Recovery rates of PCT standards for vegetable oil matrix after performing the four column clean-up procedure.
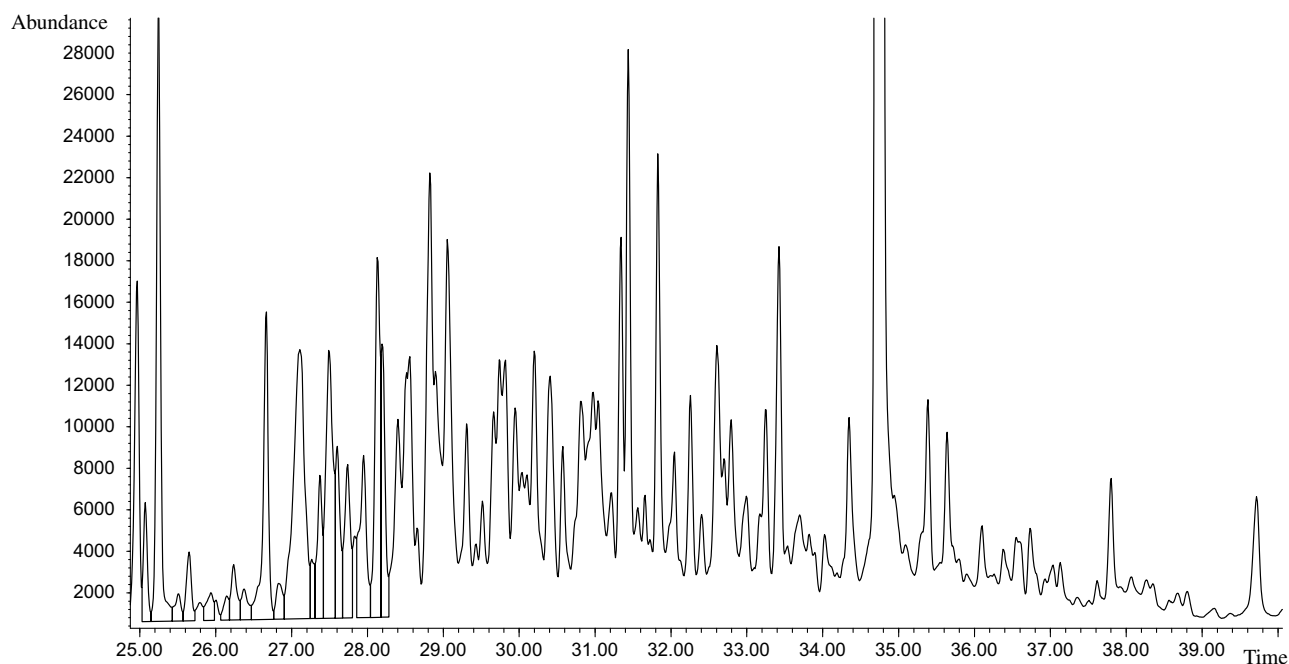
By GC/MS measurement in SCAN mode it was shown that a small amount of matrix constituents had passed the clean-up. Nevertheless, they did not disturb PCT quantification performed in selected ion mode (SIM).

3.2. PCT analysis in charcoal

From the charcoal as matrix, pyrolysis products were released during extraction. Most of these compounds were removed by the column chromatography. Therefore, no interferences on GC/MS measurements were noticed. As depicted in Fig. 2, the recovery rates of the coplanar PCT in fraction 2 were excellent. Even the non-coplanar PCT were sufficiently found in fraction 1.

3.3. PCT analysis in soil

As can be seen from Fig. 3, the analysis of PCT in soil was successful as well, as with fat or charcoal matrices, including sufficient recovery rates in both fractions. Low concentrations of some of the non-coplanar PCT in fraction 2 did not disturb the detection of the coplanar PCT target compounds.

3.4. Comparison of analytical results

For the further validation, this analytical method was performed independently by three different coworkers at least twice with all the three spiked test matrices, respectively. The resulting average recovery rates are listed in Table 3. All experiments were run with the four step clean-up procedure.

The practical limits of quantification for single PCT congeners can be named here as about 100 ng kg^{-1} for soil matrix, 200 ng kg^{-1} for charcoal matrix and 1 µg kg^{-1} for fat matrix. At least, this depends on the weighed portion of the samples, the performances of the clean-up procedure (MS: signal to noise ratio $\geqslant$10), the lowest standard solution used for external calibration and the capacity of the mass spectrometer.

3.5. Detection of PCT in combustion residues from a fire accident

It is well known, that PCDD, PCDF and PCB are easily formed in case of fire with electric cables involved, consisting of PVC and copper. In this context, the formation of the closely related PCT was expected, too. Therefore, a sample of burnt PVC cable coatings from a real fire accident was analyzed. One part of the sample was spiked with 100 µL of PCT standard mixture (20 µg mL^{-1}) containing PCT 2, 3, 14 and 15, the other part was left unspiked. After soxhlet extraction, the analytical procedure was performed as described in Section 2.

The GC/MS was run in SCAN and SIM mode. In the first florisil fraction, chlorinated compounds like PCB and polychlorinated naphthalenes were found. In the second florisil fraction PCDD and PCDF could be detected. Hints to the presence of these compounds were gained by comparison of the measured mass spectra with those of the NIST mass spectra library. In SCAN mode there were also signals present in the chromatograms, which could be assigned to PCT according to their mass spectra and retention times. In the more sensitive SIM mode, the three identified coplanar tetrachloro- and pentachloro-terphenyls were quantified, resulting in a total concentration of 17 µg kg^{-1} burnt cable coatings.

The availability of more standard reference compounds is still desirable for a really doubtless identification and a precise quantification of the pollutants. In total, 29 signals of di- to hexachlorinated non-coplanar terphenyls were identified. This must not be the total number of congeners as the peaks might represent more than just one congener, respectively. Nevertheless, by this preliminary analysis, strong indications to the possible formation of well measurable amounts of PCT during combustion processes and fire accidents were given. As an example, chromatogram cuttings of hexachlorinated non-coplanar terphenyls (florisil column, fraction 1) and tetrachlorinated coplanar terphenyls (florisil column, fraction 2) are shown in Fig. 4.

By the analysis of the sample, which was spiked with PCT 2, 3, 14 and 15 for quality control, it was shown that the separation of PCT in coplanar and non-coplanar congeners from this more

complex matrix was successful with the described clean-up procedure, too.

4. Conclusions

It could be shown that the clean-up procedure described here with two alumina columns, one mixed silicagel column, and one florisil column as the last step for the separation of PCT congeners leads to good recovery rates of the coplanar PCT with more than one chlorine atom. This was realized for the analyses of 16 PCT congeners in soil, charcoal, and vegetable oil. Nevertheless, this clean-up procedure should be considered as a modular one. Depending on the kind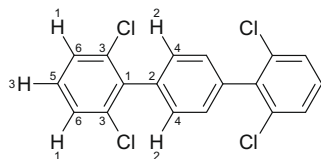 of the matrix the second alumina column could be omitted or even further clean-up steps, like a second mixed silicagel column or a third alumina column could be added.

With regard to the presented results, the analytical method should be considered as suitable for practical PCT determination in matrices from different environmental sources. Nevertheless, by the analysis of the burnt cable coatings (Section 3.5) it became obvious that there is still a demand for the availability of more coplanar congeners that could ensure a precise identification and quantification of the PCT occuring in environmental samples. In context with the analytical method presented here, a renaissance of PCT analysis can be expected, when all coplanar PCT congeners, at least with a chlorination degree of 4–7, will be available (perhaps even as ^{13}C labelled compounds). The work will be continued this way.
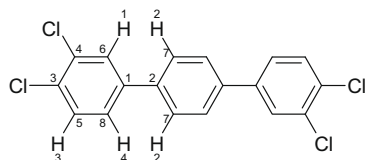
Appendix A. Spectroscopic data of PCT congeners

2,2″,6,6″-Tetrachloro-p-terphenyl
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.43 (d, J = 7.95 Hz, 4H); H-2: δ = 7.35 (s, 4H); H-3: δ = 7.24 (t, J = 7.95 Hz, 2H).

^{13}C-NMR:

C-1: δ = 139.30; C-2: δ = 136.55; C-3: δ = 135.00; C-4: δ = 129.42; C-5: δ = 129.07; C-6: δ = 128.10.
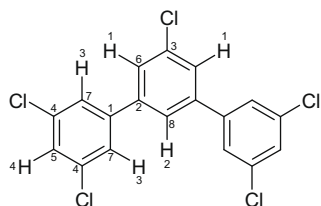
3,3″,4,4″-Tetrachloro-p-terphenyl
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.71 (d, J = 2.1 Hz, 2H); H-2: δ = 7.625 (s, 4H); H-3: δ = 7.525 (d, J = 8.3 Hz, 2H); H-4: δ = 7.45 (dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 2H).

^{13}C-NMR:

C-1: δ = 140.35; C-2: δ = 138.51; C-3: δ = 133.03; C-4: δ = 131.81; C-5: δ = 130.82;

C-6: δ = 128.85; C-7: δ = 127.54; C-8: δ = 126.24.
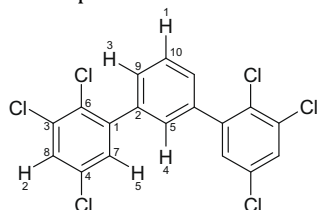
3,3″,5,5′,5″-Pentachloro-m-terphenyl
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.588 (d, J = 1.56 Hz, 2H); H-2: δ = 7.573 (t, J = 1.57 Hz, 1H); H-3: δ = 7.515 (d, J = 1.82 Hz, 4H); H-4: δ = 7.45 (d, J = 1.82 Hz, 2H).

^{13}C-NMR:

C-1: δ = 142.30; C-2: δ = 141.13; C-3: δ = 135.76; C-4: δ = 135.67; C-5: δ = 128.20;

C-6: δ = 127.09; C-7: δ = 125.75; C-8: δ = 124.14.
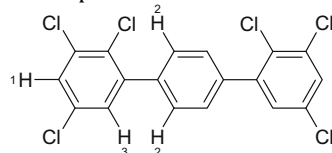
2,2″,3,3″,5,5″-Hexachloro-m-terphenyl
FTIR (cm^{-1}, gas phase): 1553, 1404, 1117, 1043, 866, 829.
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.53 (td, J1 = 7.74 Hz, J2 = 0.56 Hz, 1H); H-2: δ = 7.50 (d, J = 2.48 Hz, 2H); H-3: δ = 7.44 (dd, J1 = 7.74 Hz, J2 = 1.83 Hz, 2H); H-4: δ = 7.42 (td, J1 = 1.83 Hz, J2 = 0.56 Hz, 1H); H-5: δ = 7.29 (d, J = 2.48 Hz, 2H).

^{13}C-NMR:

C-1: δ = 142.96; C-2: δ = 138.22; C-3: δ = 134.48; C-4: δ = 132.61; C-5: δ = 129.96; C-6: δ = 129.85, C-7: δ = 129.51; C-8: δ = 129.37; C-9: δ = 129.11; C-10: δ = 128.36.
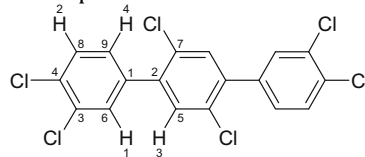
2,2″,3,3″,5,5″-Hexachloro-p-terphenyl
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.04 (d, J = 2.47 Hz, 2H); H-2: δ = 6.96 (s, 4H); H-3: δ = 6.81 (d, J = 2.48 Hz, 2H).

^{13}C-NMR:

No data, solubility is too poor.

2′,3,3″,4,4″,5′-Hexachloro-p-terphenyl
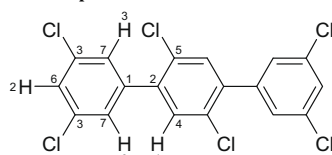FTIR (cm^{-1}, gas phase): 1454, 1133, 1036, 818.
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.56 (d, J = 8.45 Hz, 2H); H-2: δ = 7.55 (d, J = 8.45 Hz, 2H); H-3: δ = 7.45 (s, 2H); H-4: δ = 7.32 (d, J1 = 8.45 Hz, J2 = 2.09 Hz, 2H).

^{13}C-NMR:

C-1: δ = 138.97; C-2: δ = 137.31; C-3: δ = 132.77; C-4: δ = 132.58; C-5: δ = 132.18; C-6: δ = 131.15; C-7: δ = 131.00, C-8: δ = 130.34; C-9: δ = 128.66.
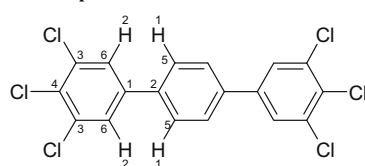
2′,3,3″,5,5′,5″-Hexachloro-p-terphenyl
FTIR (cm^{-1}, gas phase): 1587, 1563, 1488, 1417, 1101, 1059, 862, 806.
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.48 (s, 2H); H-2: δ = 7.43 (d, J = 1.90 Hz, 2H); H-3: δ = 7.35 (d, J = 1.90 Hz, 4H).

^{13}C-NMR:

C-1: δ = 140.15; C-2: δ = 138.96; C-3: δ = 134.98; C-4: δ = 132.19; C-5: δ = 131.02; C-6: δ = 128.50; C-7: δ = 127.80.

3,3″,4,4″,5,5″-Hexachloro-p-terphenyl
NMR-spectra:

^{1}H-NMR:

H-1: δ = 7.635 (s, 4H); H-2: δ = 7.625 (s, 4H).

^{13}C-NMR:

C-1: δ = 140.48; C-2: δ = 138.25; C-3: δ = 135.0; C-4: δ = 131.02; C-5: δ = 127.95; C-6: δ = 127.42.

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