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Application of correlation analysis for identification of polychlorinated biphenyls

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Abstract

The analytical process was optimized for the determination of individual PCBs in a commercial mixture, Delor 104, and in soil samples contaminated by PCBs. The optimal analytical conditions for the GC–MS system with a DB-5 capillary column involved a temperature program evaluated in terms of information content $I(S)$ and information flow $I(S)/t$ and an identification procedure based on the correlation analysis of the measured and published relative retention $r_{1,2}$ data.

Keywords: Correlation analysis; Environmental analysis; Polychlorinated biphenyls

1. Introduction

The composition of PCB-containing samples in the environment continuously changes due to natural degradation processes [1]. The knowledge of the composition of PCBs contained in samples is mandatory for studying their toxic effects, biodegradation processes and for environmental monitoring. There are 209 PCB congeners and they are usually analyzed by gas chromatography with electron-capture (ECD) and mass spectrometric detection [2,3].

The main practical problem for PCB analysis is linked with the lack of a complete set of individual standards. Commercial mixtures of PCBs are usually employed as standards for qualitative and quantitative analysis. Since the PCB composition of environmental samples differs from that in the stan-

dards available, analyses related to individual congeners are required.

Coelution of some 209 PCB congeners on a single capillary column can also be a source of problems [4–8] (only multi-dimensional chromatography permits complete separations of PCBs [3,9]).

The aim of our work was to obtain a maximum amount of information on the PCB composition in environmental samples by applying correlation analysis between commercial PCB standard mixtures and the retention data cited in the literature.

2. Experimental

2.1. Chemicals

PCBs commercial mixtures Delor 103, 104, 106 (corresponding, in the degree of chlorination, to Aroclor 1242, 1248, 1260, respectively) were ob-

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tained from Chemko Strážské (Slovak Republic) (a concentration of $1 \mu\text{g } \mu\text{l}^{-1}$); octachloronaphthalene (OCN) came from the Labor Dr. Ehrenstorfer (Augsburg, Germany) (a concentration of $10 \text{ ng } \mu\text{l}^{-1}$) and soil samples contaminated by PCBs (without information on the origin of contamination) came from the Macadam Plant (Milevsko, Czech Republic) (a declared concentration of $45 \mu\text{g Delor 103 per g}$ of sample). The solvents used were *n*-heptane, acetone and hexane, analytical grade, from Lachema (Brno, Czech Republic).

2.2. Preparation of soil samples

The white rot fungi (*Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Trametes versicolor* and *Coriolopsis polyzona*), grown 3 weeks on a sterilized straw (125 g), were applied to 500 g of the soil sample for a biodegradation test. The samples placed in aluminium foil-covered vessels were incubated at 27°C and 85% humidity and were sprayed with water once a week.

After 10 months, homogenized soil samples (5 g) were extracted in a Soxhlet apparatus with a hexane–acetone (3:1) mixture for 4 h, filtered through a cotton wool and washed with acetone. The organic solvent portion was back-extracted with concentrated sulfuric acid (to decoloration) and then with distilled water (to neutral pH), and filtered through a layer of anhydrous sodium sulfate to remove water residues. Finally, the organic portion was evaporated on a rotary evaporator to preconcentrate PCBs and the residue was dissolved in $200 \mu\text{l}$ *n*-heptane. The recovery of the extraction was approximately 90%.

2.3. GC–MS

The analyses of PCBs were performed on a high-resolution gas chromatograph, Model Varian 3400 (Zug, Switzerland) with a Finnigan Mat 800 ion-trap detector (San Jose, CA, USA). A DB-5 capillary column (J&W Scientific, Folsom, CA, USA), $29 \text{ m} \times 0.25 \text{ mm I.D.}$, with a film thickness of $0.25 \mu\text{m}$, was used. The capillary column was tested with tetradecane at 125°C, obtaining a solute capacity factor of $k' = 7.025$ and a number of theoretical plates of 3900 per meter. Helium was employed as the

Table 1

Temperature conditions of GC–MS analysis of PCBs (suitable conditions to obtain linear equation are in bold letters)

80°C/0.5 min/25°C min ⁻¹ /100°C/1°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /100°C/2°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /100°C/2.5°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /100°C/3°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /125°C/1°C min ⁻¹ /290°C
80°C/0.5 min/25°C min⁻¹/125°C/2°C min⁻¹/290°C
80°C/0.5 min/25°C min ⁻¹ /125°C/3°C min ⁻¹ /290°C
80°C/0.5 min/25°C min⁻¹/140°C/3°C min⁻¹/290°C
80°C/0.5 min/25°C min ⁻¹ /150°C/1°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /150°C/2°C min ⁻¹ /290°C
80°C/0.5 min/25°C min⁻¹/150°C/3°C min⁻¹/290°C
80°C/0.5 min/25°C min ⁻¹ /180°C/1°C min ⁻¹ /290°C
80°C/0.5 min/25°C min ⁻¹ /180°C/2°C min ⁻¹ /290°C

carrier gas with a linear velocity of 10 cm s^{-1} , as measured at 80°C. All the measurements were carried out in a full-scan mode, with a mass range from 150 to 450 *m/z*. The injected sample volume was $1 \mu\text{l}$ in the splitless mode; the temperature program initiated at 80°C for 0.5 min, with a fast gradient of $25^\circ\text{C min}^{-1}$ to the start temperature T_s , equal to 100, 125, 140 or 150°C, followed by a gradient ΔT of 1 to 4°C min^{-1} , to the final temperature of 290°C. Under these conditions, all the PCBs eluted during the temperature gradient (for the temperature programs see Table 1). The detector and injector temperature was 250°C in all the analyses.

3. Results

3.1. Relationship between the literature and measured data

A correlation analysis of relative retention times r_{12} of PCB congeners was carried out for the data sets published by Mullin et al. [10] and Frame [11] and our experimental data for Delor 103 and Delor 106. The basic experimental conditions for the cited measurements and our measurements were similar. The composition of PCB commercial mixtures (Delor 103, 106) has already been published [12], and was later independently verified [13].

First, a correlation between Mullin's (r_{12M}) and Frame's (r_{12F}) relative retention data was carried out, finding a polynomial regression of the third

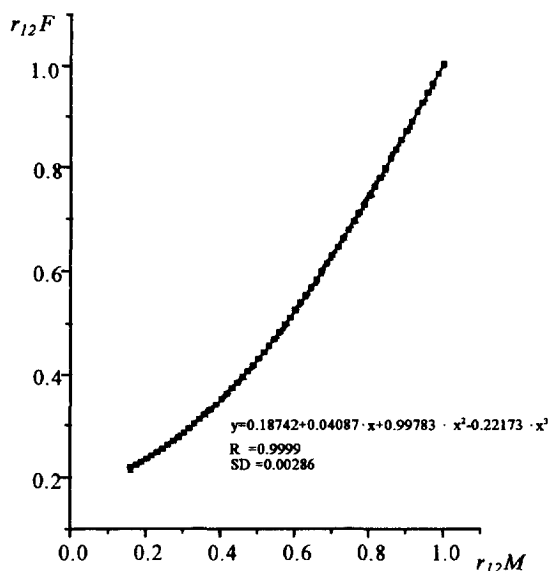


Fig. 1. Regression between the literature data $r_{12}M$ (Mullin [10]) and $r_{12}F$ (Frame [11]).

order to be the best fit (Fig. 1). Eq. (1) holds for the regression of the third order.

$$y = a_0 + a_1x + a_2x^2 + a_3x^3, \quad (1)$$

where y are the data obtained by Frame or the measured data, and x are Mullin's data.

Therefore, the polynomial regression of the third order was also applied to the analyses of our experimental r_{12} data on the Delor mixtures and Mullin's data were chosen as more suitable for the regression. These data, obtained on the basis of all individual PCB congener analyses, are supposed to be the most complete.

It was found that the values of the regression coefficients a_x depend on the optimized temperature T_s and the gradient ΔT (cf. Fig. 2, Fig. 3, Fig. 4, and Fig. 5) and for regression coefficients $a_2 \rightarrow 0$ and $a_3 \rightarrow 0$, the third order equation could be reduced to a linear equation,

$$y = a'_0 + a'_1x \quad (2)$$

A linear equation was sought to simplify the analytical method. While for a polynomial regression the retention data have to be related to the same internal standard (OCN), for linear regression t_r , they can be

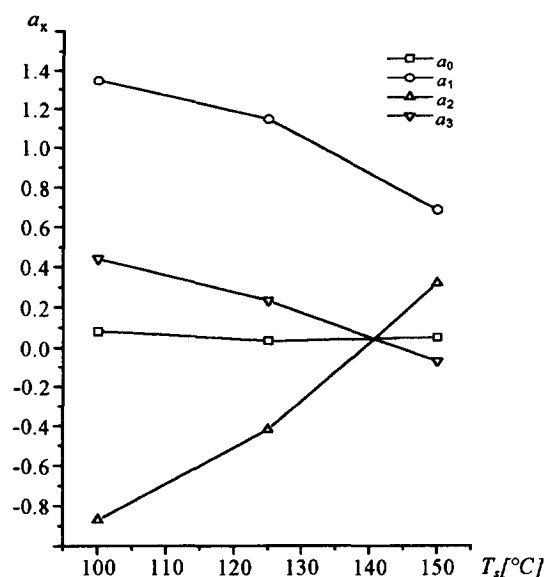


Fig. 2. Dependence of regression coefficients a_x (where x corresponds to the exponent of the independent variable $r_{12}M$) on the temperature T_s for the temperature program with $\Delta T = 3^\circ\text{C min}^{-1}$ $80^\circ\text{C}/0.5 \text{ min}/25^\circ\text{C min}^{-1}/T_s/3^\circ\text{C min}^{-1}/290^\circ\text{C}$.

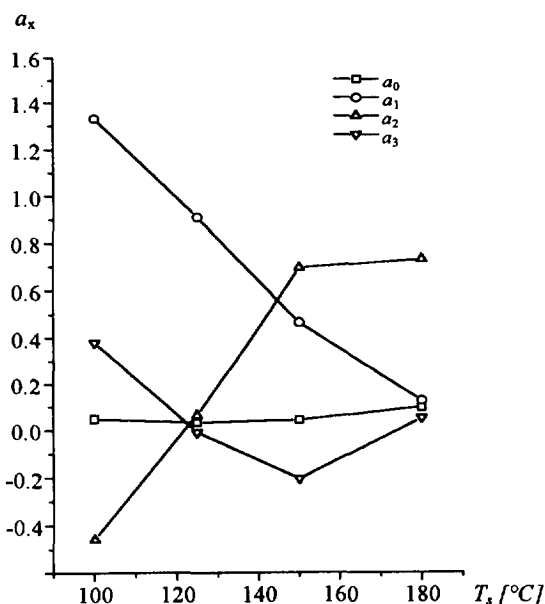


Fig. 3. Dependence of regression coefficients of the equation on the temperature T_s for the temperature program with $\Delta T = 2^\circ\text{C min}^{-1}$ (for a_x cf. Fig. 2) $80^\circ\text{C}/0.5 \text{ min}/25^\circ\text{C min}^{-1}/T_s/2^\circ\text{C min}^{-1}/290^\circ\text{C}$.

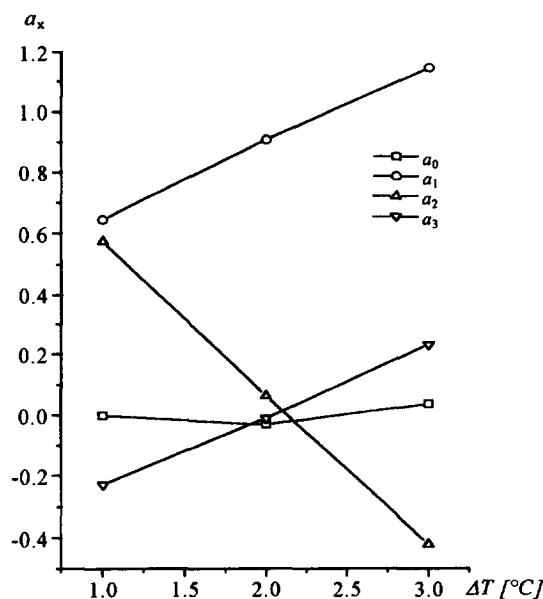


Fig. 4. Dependence of regression coefficients of the equation on temperature gradient ΔT for $T_s = 125^\circ\text{C}$ (for a_x cf. Fig. 2.) $80^\circ\text{C}/0.5 \text{ min}/25^\circ\text{C min}^{-1}/125^\circ\text{C}/\Delta T^\circ\text{C min}^{-1}/290^\circ\text{C}$.

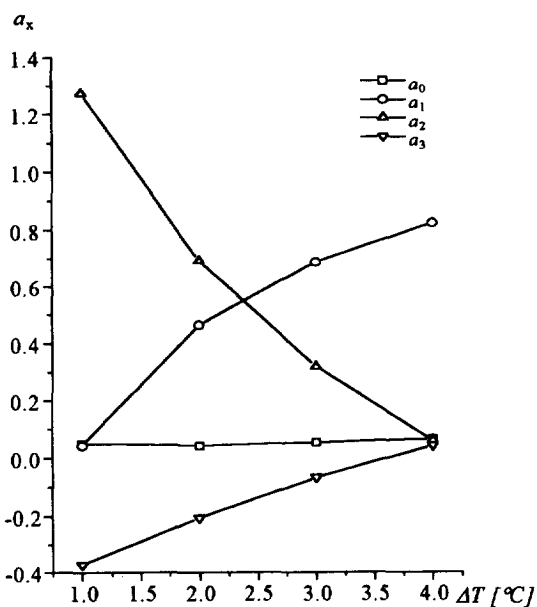


Fig. 5. Dependence of regression coefficients of the equation on temperature gradient ΔT for $T_s = 150^\circ\text{C}$ (for a_x cf. Fig. 2.) $80^\circ\text{C}/0.5 \text{ min}/25^\circ\text{C min}^{-1}/150^\circ\text{C}/\Delta T^\circ\text{C min}^{-1}/290^\circ\text{C}$.

related to any compound in the sample. The temperature conditions were optimized in terms of the parallel validity of the linear relationship of the relative retention according to Eq. (2) and the maximum value of information content $I(S)$ and information flow $I(S)/t$ for analyses of Delor 104 (see Section 3.2).

The suitable temperature programs were determined by plotting the regression coefficients a_x versus the start temperature T_s (Figs. 2 and 3) and versus the temperature gradient ΔT (Figs. 4 and 5). Fig. 2 indicates that the start temperature $T_s = 140^\circ\text{C}$ is the optimum for the gradient $\Delta T = 3^\circ\text{C min}^{-1}$, while the start temperature $T_s = 125^\circ\text{C}$ is the optimum for the gradient $\Delta T = 2^\circ\text{C min}^{-1}$ (Fig. 3). Table 2 gives the regression coefficients a_x of the polynomial and a'_x of the reduced linear equation at different temperature conditions. The most suitable temperature programs are shown in bold letters in Table 1.

3.2. Analyses of Delor 104

The sample of Delor 104 with internal standard OCN ($r_{12} = 1$) was analyzed under 3 selected temperature programs and polynomial and linear regression were determined (Table 2). Grubb's outlier test was applied to test the suitability of these equations for the identification of all of the PCBs. The procedure was as follows: The measured retention times (t_r) were recalculated according to the relative retention related to OCN (r_{12}) and the chlorine number (Cl) was determined from the mass spectra (Table 3). A confidence interval ($r_{12\text{min}}, r_{12\text{max}}$) was calculated for r_{12} and in the column PCBs (Table 3) polychlorinated biphenyls were ordered which fitted into the confidence interval. The PCBs, which also correspond to the degree of chlorination obtained from the mass spectra, are typed bold. Next, Mullin's r_{12} scale was divided into 1% compartments (Table 4) and linked with the r_{12} confidence interval of the PCB congeners in the commercial mixtures. The data in Table 4 were used to identify the probable PCBs in Table 3.

Based on the analysis of Delor 104, the three temperature programs were compared in terms of the information content $I(S)$, Eq. (3), and the information flow $I(S)/t$, Eq. (4); refer to Table 2.

Table 2
PCB identification in Delor 104 on the basis of three optimal temperature programs

T_s	125°C	140°C	150°C
ΔT	2°C min ⁻¹	3°C min ⁻¹	4°C min ⁻¹
Analysis time	66 min	46 min	35 min
Number of peaks in chromatogram	88	86	86
PCB identification polynomial eq.	0.014 + 1.004x + 0.099x ² + 0.076x ³	0.039 + 0.867x + 0.063x ² + 0.024x ³	0.068 + 0.792x + 0.134x ² - 0.008x ³
S.D.	0.00219	0.00218	0.00200
Identified PCBs	117	115	118
PCBs out of confidence interval	2	5	8
PCB identification linear eq.	0.0153 + 0.9717x	0.0100 + 0.9680x	0.0321 + 0.9372x
S.D.	0.00263	0.00382	0.0063
Identified PCBs	118	117	117
PCBs out of confidence interval	2	5	15
$I(S)$	8.8464	7.4138	5.8293
$I(S)/t$	0.1246	0.1454	0.1457

$$I(S) = \sum_z P_i \ln P_i - \ln E \quad (3)$$

where P_i is the probability of identification of component i ; in a mixture of Z compounds, $P_i = 1/Z$ and E represents the PCBs found out of the confidence interval.

$$I(S)/t = I(S)/(t_{r_{\max}} + t_{\text{reset}}) \quad (4)$$

where $t_{r_{\max}}$ is the retention time of the last eluting PCB and t_{reset} is the time required for commencing the next analysis.

3.3. Analyses of soil samples

The goal of our analysis was a quantitative determination of the biodegradation efficiency for individual PCBs in the soil samples. The extracts of soil samples were analyzed under the temperature program with $T_s = 140^\circ\text{C}$ and $\Delta T = 3^\circ\text{C min}^{-1}$. Differences in PCB composition of the soil sample, Delor 103 and Delor 104 can be seen from the chromatograms (Fig. 6). The soil sample PCB congeners were identified using the procedure in Section 3.2 and it was confirmed that the congeners relate completely neither to Delor 103 nor to Delor 104 (Table 5). To check the evaporation of PCBs from soil samples, three flasks with soil were contaminated with PCBs and left open in the fume cupboard under ambient conditions. The soil was extracted after 1 month on a Soxhlet apparatus and

analyzed by GC-ECD. No significant evaporation was observed.

4. Discussion

Suitable conditions for fast and efficient PCB separation and a linear relationship of r_{12} to the published data were obtained (Table 2). For the temperature programs beginning at $T_s = 100^\circ\text{C}$ and $T_s = 180^\circ\text{C}$, no optimal gradients were found. Furthermore, the analysis would be time-consuming at the low temperature (135 min), whereas the polynomial function could not be reduced into a linear one at high T_s .

The data from Table 2 demonstrate that the greatest amount of information is obtained for the temperature program with $T_s = 125^\circ\text{C}$, $\Delta T = 2^\circ\text{C min}^{-1}$; however, this is the program with the lowest information flow $I(S)/t$. Under the program $T_s = 140^\circ\text{C}$, $\Delta T = 3^\circ\text{C min}^{-1}$, the value of information flow $I(S)/t$ was approximately equal to $I(S)/t$ for the program $T_s = 150^\circ\text{C}$, $\Delta T = 4^\circ\text{C min}^{-1}$. The information content $I(S)$ is higher for the program $T_s = 140^\circ\text{C}$, $\Delta T = 3^\circ\text{C min}^{-1}$; therefore, it is assumed that this program will permit complete identification of the biodegradation products.

The programs used for analysis of Delor 104 are compared in Table 2. Identification of the last eluting PCB isomers of a particular chlorination level was very often found to be outside the confidence interval

Table 3

Example of identification procedure for Delor 104 for temperature program 80°C/0.5 min/25°C min⁻¹/140°C/3°C min⁻¹/290°C, where (r_{12min} , r_{12max}) is the confidence interval for r_{12} ; $S.D.=0.00382$ is obtained from linear regression

t_r	Cl	r_{12}	r_{12min}	r_{12max}	PCBs expected on the basis of the confidence interval ^a	Probable PCBs ^a
420	0	0.1265	0.1189	0.1342		biphenyl
550	1	0.1749	0.1673	0.1826		1
663	1	0.2170	0.2093	0.2246	10, 4	3
719	2	0.2378	0.2302	0.2455		10, 4
796	2	0.2665	0.2588	0.2741	7, 9, 6	7, 9
828	2	0.2784	0.2707	0.2860	6, 8, 5	6
854	2	0.2881	0.2804	0.2957		8, 5
908	3	0.3082	0.3005	0.3158	19	19
997	3	0.3413	0.3336	0.3489	18, 15, 17	18
1003	3	0.3435	0.3359	0.3511	18, 15, 17, 24, 27	17
1014	2	0.3476	0.3400	0.3552	24, 27	15
1023	3	0.3509	0.3433	0.3586	24, 27	24, 27
1056	3	0.3632	0.3556	0.3709	16, 32	16
1061	3	0.3651	0.3575	0.3727	16, 32	32
1086	3	0.3744	0.3668	0.3820	23, 34, 54, 29	34
1100	4 + 3	0.3796	0.3720	0.3872	23, 34, 54, 29	54, 29
1129	3	0.3904	0.3828	0.3980	26, 25, 50	26
1132	3	0.3915	0.3839	0.3992	26, 25, 50	25
1174	3	0.4071	0.3995	0.4148	31, 28, 21, 33, 20	31, 28
1201	3	0.4172	0.4096	0.4248	28, 21, 33, 20, 53, 51, 22	21, 33
1212	4	0.4213	0.4136	0.4289	20, 53, 51, 22	51
1228	3	0.4272	0.4196	0.4349	51, 22, 45, 36	22
1236	4	0.4302	0.4226	0.4379	22, 45, 36	45
1260	4	0.4392	0.4315	0.4468	36, 46, 39, 69	46
1297	4	0.4529	0.4453	0.4606	69, 73, 52, 43, 38, 49, 47, 75, 48	52, 43
1310	4	0.4578	0.4501	0.4654	73, 52, 43, 38, 49, 47, 75, 48, 65, 62	49
1318	4	0.4607	0.4531	0.4684	43, 38, 49, 47, 75, 48, 65, 62, 35	48, 47
1366	4	0.4786	0.4710	0.4862	44, 37, 59, 42	44
1374	4	0.4816	0.4739	0.4892	44, 37, 59, 42	42
1389	3	0.4872	0.4795	0.4948	37, 59, 42, 72, 71, 41, 64	37
1403	4	0.4924	0.4847	0.5000	72, 71, 41, 64, 68, 96	72, 71, 41
1412	4	0.4957	0.4881	0.5034	72, 71, 41, 64, 68, 96	64
1431	4	0.5028	0.4952	0.5104	68, 96, 40, 103, 57	40
1459	4	0.5132	0.5056	0.5209	103, 57, 100, 67, 58	67
1481	4	0.5214	0.5138	0.5290	100, 67, 58, 63, 61, 94, 74	58, 63
1501	4	0.5288	0.5212	0.5365	63, 61, 94, 74, 70, 76, 98, 102, 93	74
1528	4	0.5389	0.5313	0.5465	70, 76, 98, 102, 93, 66, 95, 80, 88, 121	70, 76
1536	5 + 4	0.5419	0.5342	0.5495	98, 102, 93, 66, 95, 80, 88, 121, 91, 55	66, 95
1547	5	0.5460	0.5383	0.5536	95, 80, 88, 121, 91, 55	91
1554	4	0.5486	0.5409	0.5562	88, 121, 91, 55	55
1591	4	0.5623	0.5547	0.5700	155, 56, 60, 92, 84, 89	56, 60
1595	5	0.5638	0.5562	0.5715	155, 56, 60, 92, 84, 89	92, 84, 89
1600	5	0.5657	0.5580	0.5733	155, 56, 60, 92, 84, 89, 90, 101	89
1622	5	0.5739	0.5662	0.5815	89, 90, 101, 113, 99, 79	90, 101
1633	5	0.5780	0.5703	0.5856	90, 101, 113, 99, 79	113, 99
1664	5	0.5895	0.5819	0.5971	119, 150, 112, 109, 78, 83, 152	109, 83
1686	5	0.5977	0.5901	0.6053	109, 78, 83, 152, 97, 86, 116, 125, 81, 145, 117	97
1713	5	0.6077	0.6001	0.6154	86, 116, 125, 81, 145, 117, 115, 87, 111, 85, 148	87, 111
1724	5	0.6118	0.6042	0.6195	125, 81, 145, 117, 115, 87, 111, 85, 148, 120, 136, 77	120
1733	6	0.6152	0.6075	0.6228	115, 87, 111, 85, 148, 120, 136, 77, 110	148

Table 3. Continued

t_r	Cl	r_{12}	r_{12min}	r_{12max}	PCBs expected on the basis of the confidence interval ^a	Probable PCBs ^a
1749	5	0.6211	0.6135	0.6288	148, 120 , 136, 77, 110 , 154	110
1758	4	0.6245	0.6168	0.6321	77 , 110, 154, 82	77
1782	5	0.6334	0.6258	0.6411	154, 82 , 151	82
1791	6	0.6368	0.6291	0.6444	82 , 151	151
1808	6	0.6431	0.6355	0.6507	151 , 135 , 144 , 124, 147	135
1815	6	0.6457	0.6381	0.6533	151 , 135 , 144 , 124, 147 , 108, 107	144
1841	6	0.6554	0.6477	0.6630	147 , 108, 107, 123, 149 , 106, 118, 139 , 140	149
1856	5	0.6610	0.6533	0.6686	123 , 149, 106 , 118 , 139, 140, 143, 134	118
1869	6	0.6658	0.6582	0.6734	139 , 140 , 143 , 134 , 114, 142 , 131	143, 134
1884	6	0.6714	0.6637	0.6790	143 , 134 , 114, 142 , 131 , 122 , 133	131
1911	6	0.6814	0.6738	0.6891	131 , 122 , 133 , 165 , 188, 146 , 161	146
1943	6	0.6933	0.6857	0.7010	184, 132 , 153 , 105, 168 , 127, 141 , 179	132, 153
1947	5	0.6948	0.6872	0.7025	184, 132, 153, 105 , 168, 127	105
1978	7	0.7064	0.6987	0.7140	141, 179	179
1984	6	0.7086	0.7010	0.7162	141 , 179	141
2006	7	0.7168	0.7091	0.7244	176 , 137	176
2010	6	0.7183	0.7106	0.7259	176, 137	137
2034	6	0.7272	0.7196	0.7348	160 , 163 , 164 , 138 , 186, 158	160, 163, 164
2042	6	0.7302	0.7225	0.7378	160 , 163 , 164 , 138 , 186, 158 , 129 , 126	138, 158
2058	7	0.7361	0.7285	0.7438	158, 129, 126, 178 , 166	178
2094	7	0.7495	0.7419	0.7572	166, 175 , 182 , 187 , 159, 183	182, 187
2114	7	0.7570	0.7493	0.7646	182 , 187 , 159, 183 , 162, 128	183
2132	6	0.7637	0.7560	0.7713	183, 162 , 128 , 167 , 185	128
2147	6	0.7693	0.7616	0.7769	128 , 167 , 185	167
2151	8	0.7707	0.7631	0.7784	167, 185	185
2180	7	0.7815	0.7739	0.7892	174 , 181 , 177	174
2198	7	0.7882	0.7806	0.7959	174 , 181 , 177 , 171 , 202, 156	177
2215	7	0.7946	0.7869	0.8022	177 , 171 , 202, 156, 173 , 157	171
2228	6	0.7994	0.7918	0.8070	171, 202, 156 , 173, 157 , 200, 204	156
2263	7	0.8124	0.8048	0.8201	204, 192 , 172 , 197, 180	172
2295	7	0.8243	0.8167	0.8320	180 , 193 , 191	180
2394	7	0.8612	0.8535	0.8688	170 , 190 , 198	170, 190
2422	8	0.8716	0.8640	0.8792	198 , 201 , 196 , 203	198, 201
2445	8	0.8802	0.8725	0.8878	196 , 203	196, 203
2551	8	0.9196	0.9120	0.9273	195 , 207	195
2634	8	0.9505	0.9429	0.9581	205	194, 205

^a Systematic numbering of PCBs according IUPAC nomenclature.

(coplanar PCBs are among these analytes). Furthermore, Mullin found the PCB elution order 18, 15, 17, while we found PCB No. 15 eluting last of this group. The most probable reason for this difference is the different polarities of the stationary phases used [3–8].

Identification of some mono- and dichlorinated PCBs under the temperature program with $T_s = 140^\circ\text{C}$ and $\Delta T = 3^\circ\text{C}$ and using the linear regression of r_{12} , was found to be out of the confidence interval. Because there are a few low-chlorinated PCBs, they can be identified by the mass spectra, and with the

help of the data in Table 4. Although identification of PCBs is slightly worse when using the linear equation than at $T_s = 125^\circ\text{C}$, $\Delta T = 2^\circ\text{C}$, the higher temperature shortens the analysis time and is more suitable for common laboratory practice.

When using a high start temperature, identification of mono-, octa- and nona-chlorinated congeners becomes difficult. Identification would require a polynomial regression, while the linear one would only be acceptable for analyses of a narrow range of tri- to hepta-chlorinated biphenyls.

The chromatograms in Fig. 6 and the data in Table

Table 4

PCBs divided into 1% relative retention time compartments and selection of PCBs found in commercial mixtures

PCBs ^a	PCBs present in commercial mixtures ^a	PCBs ^a	PCBs present in commercial mixtures ^a
1	1	90, 101, 113, 99, 79	90, 101, 113, 99
2, 3	3	119, 150, 112	119
10, 4	4	109, 78, 83, 152	83
7, 9	7, 9	97, 86, 116, 125, 81, 145, 117, 115, 87, 111	97, 87, 115, 111
6, 8, 5	6, 8, 5	85, 148, 120, 136, 77	148, 77, 136
14		110, 154, 82, 151	110, 82, 151
19	19	135, 144, 124	135, 144
30		147, 108, 107, 123, 149, 106, 118	107, 108, 123, 147, 118
11, 12		139, 140, 143, 134	143, 134
13, 18, 15, 17	13, 15, 18, 17	114, 142, 131, 122, 133	114, 131
24, 27	24, 27	165, 188, 146, 161	146
16	16	184, 132, 153, 105, 168, 127	132, 153, 105
32	32	141, 179, 130	141, 179, 130
23		176, 137, 160, 163, 164	176, 137, 160, 163, 164
34	34	138, 186, 158	163, 138, 158
54, 29	29	129, 126, 178, 166	126, 129, 178
26, 25	26, 25	175, 182, 187, 159	175, 182, 187, 159
50, 31, 28	31, 28	183, 162, 128	183, 128, 162
21, 33, 20, 53	20, 33, 53	167, 185	167, 185
51, 22	51, 22	174, 181	174
45, 36	45	177, 171, 202	177, 171
46, 39	46	156, 173, 157, 200	156, 157, 200
69, 73, 52, 43, 38	52, 43	204, 192, 172, 197	192, 172, 197
49, 47, 75, 48, 65, 62	49, 48, 47	180, 193	180, 193
35, 104	35	191, 199	191, 199
44, 37, 59, 42	44, 37, 42	169	
72, 71, 41, 64	72, 71, 41, 64	170, 190	170, 190
68, 96		198, 201	198, 201
40, 103, 57	40, 103	196, 203	196, 203
100, 67, 58, 63	100, 67, 63, 58	189	189
61, 94, 74	94, 74	208, 195	208, 195
70, 76, 98, 102, 93, 66, 95, 80, 88	70, 76, 95, 66, 80	207	207
121, 91, 55	91, 55	194, 205	194, 205
155, 56, 60	56, 90	206	
92, 84, 89	92, 84, 89	209	

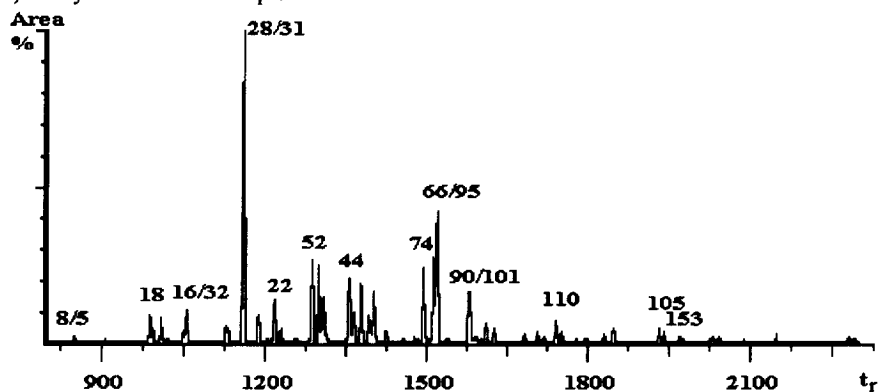
^a Systematic numbering of PCBs according IUPAC nomenclature.

5 indicate that soil samples provide PCB composition patterns that are different from those of commercial mixtures Delor 103 and Delor 104. Thus, the analysis performed on the basis of major components (usual in practice) does not provide information on PCB biodegradation of samples and the congener-specific analysis is mandatory.

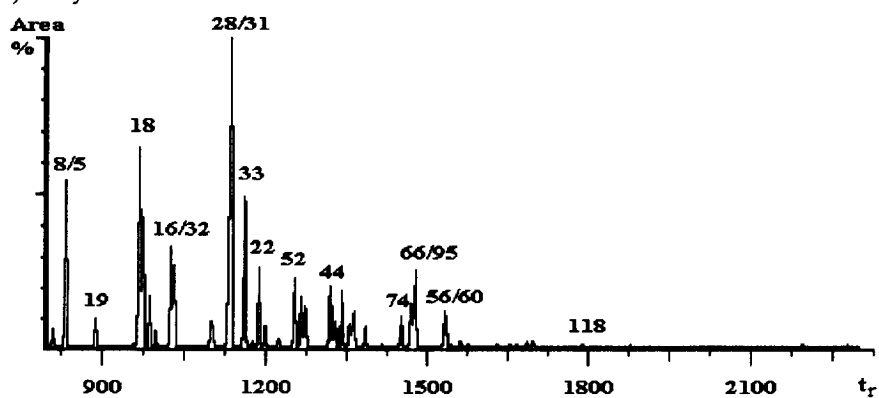
We assume that the samples were originally contaminated by Delor 103, as Delor 104 contains more high-chlorinated biphenyls, which are more

resistant to natural degradation than low-chlorinated ones that predominate in Delor 103. Compared to the two commercial mixtures, we conclude that di- and trichlorinated biphenyls in the soil samples were degraded, including the congeners: 10, 4, 7/9, 6, 8/5, 19, 18, 17, 15, 16, 32, 33. The possibility of the selective PCB evaporation from a liquid media was reported [14]. Our results on soil evaporation (refer to Section 3.3) as well as the results of a controlled PCB standard evaporation in the vacuum rotary

a) Analyses of the soil sample



b) Analyses of Delor 103



c) Analyses of Delor 104

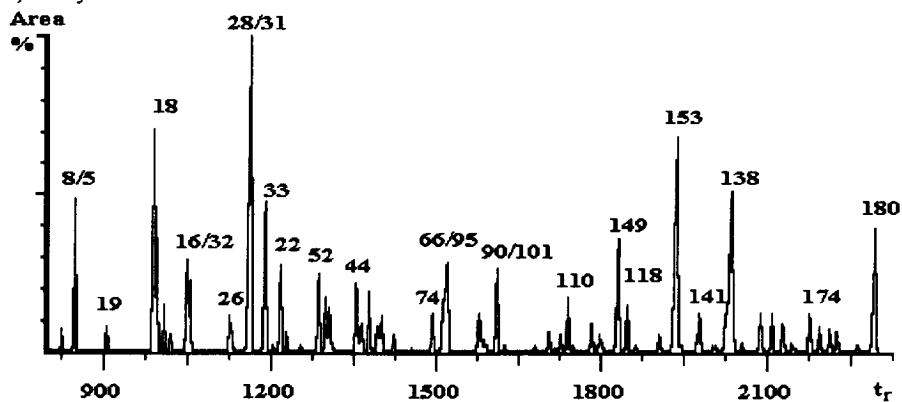


Fig. 6. Comparison of analyses on GC-MS under temperature program $80^{\circ}\text{C}/0.5\text{ min}/25^{\circ}\text{C min}^{-1}/140^{\circ}\text{C}/3^{\circ}\text{C min}^{-1}/290^{\circ}\text{C}$.

Table 5
Comparison of peak areas (%) for identified PCBs congeners

PCBs	Soil samples Area %	Delor 103 Area %	Delor 104 Area %	PCBs	Soil samples Area %	Delor 103 Area %	Delor 104 Area %
1	0.03	0.09	0.08	90, 101	1.29	0.21	2.94
3		0.03	0.15	113, 99	0.94	0.16	0.53
10, 4	0.13	2.58	2.92	109, 83	0.53		0.07
7, 9		0.02	0.06	97	0.71	0.12	0.46
6	0.08	0.70	0.23	87, 111	0.46	0.02	0.76
8, 5	0.39	6.23	2.74	120		0.09	0.31
19	0.17	1.04	0.60	148			0.65
18	1.58	10.76	2.10	110	1.44	0.29	1.69
17	0.91	4.49	0.79	77	0.89	0.29	0.44
15	1.42	1.77	0.98	82	0.29	0.06	0.08
24, 27	0.31	0.60	0.39	151			1.17
16	0.67	4.36	2.94	135			0.14
32	0.28	3.17	2.22	149	0.56	0.06	3.43
34			0.02	118	1.09	0.18	1.20
54, 29			0.04	143, 134			0.14
26	1.17	1.12	0.54	131			0.08
25	0.92		0.94	146			0.42
31, 28	19.92	21.74	7.35	132, 153	0.70	0.07	4.19
21, 33		7.31	5.68	105	0.51	0.16	0.55
51	0.20	0.21	0.30	179	0.13		0.30
53	0.23			141			0.76
22	2.78	3.52	2.98	176			0.25
45	0.81	0.86	1.02	160, 163, 164	0.44		0.54
46	0.27	0.37	0.46	138, 158		0.05	3.42
52, 43	5.36	2.80	4.96	178			0.28
49	4.71	2.31	3.55	182, 187	0.07		1.11
48, 47	3.45	2.14	2.83	183	0.19		0.69
44	4.38	2.39	4.13	128			0.27
42	2.12	1.28	1.68	167			0.09
37	3.86	2.54	2.19	185			0.11
72, 71	2.25	1.60	2.23	174			0.83
64	3.54	1.65	1.29	177			0.46
40	0.85	0.75	0.88	171			0.00
67	0.26	0.07	0.15	156			0.14
58, 63	0.35	0.08	0.16	172			0.11
74	4.66	1.34	2.56	180			1.21
94	0.15			170, 190			0.68
70, 76	6.26	2.65	1.65	198, 201			0.24
66, 95	9.19	3.10	0.78	196, 203			0.28
91	0.41	0.16	0.06	195			0.07
55	0.10		0.05	194			1.51
56, 60	5.21	2.22	2.27				
92, 84	0.32	0.15	0.11				
89	0.05		0.19				

evaporator demonstrate that there is no selective PCB evaporation within one group of Cl-isomers. Thus, our finding of a selective decrease in the contents of some low chlorinated biphenyls have to be linked to biodegradation.

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References

- [1] K.C. Jones, V. Burnett, R. Duarte-Davison and K.S. Waterhouse, *Chemistry in Britain*, 5 (1991) 435.
- [2] K. Ballschmiter, Ch. Rappe and H.R. Buser, in Kimbrough and Jensen (eds.), *Halogenated biphenyls, terphenyls, naphthalens, dibenzodioxins and related products*, Elsevier Science Publishers B.V., 1989, Ch. 2, p. 47.
- [3] B.R. Larsen, *J. High Resolut. Chromatogr.*, 18 (1995) 141.
- [4] S. Bowadt, B. Larsen, *J. High Resolut. Chromatogr.*, 15 (1992) 350.
- [5] B.R. Larsen, S. Bowadt and R. Titio, *Int. J. Environ. Anal. Chem.*, 47 (1992) 47.
- [6] B.R. Larsen, S. Bowadt R. Titio and S. Facchetti, *Chemosphere*, 25 (1992) 1343.
- [7] S. Bowadt, H. Skejo, L. Montanarella and B.R. Larsen, *Int. J. Environ. Anal. Chem.*, 56 (1994) 87.
- [8] B.R. Larsen, M. Cont, L. Montanarella and N. Platzner, S. Bowadt, H. Skejo, *J. Chromatogr. A*, 708 (1995) 115.
- [9] V. Lang, *J. Chromatogr.*, 595 (1992) 1.
- [10] M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe and L.M. Safe, *Environ. Sci. Technol.*, 18 (1984) 468.
- [11] G.M. Frame, 13th Progress Report, Research and Development Program for the Destruction of PCBs, General Electrical Company, Schenectedy, New York, 1994, p. 175.
- [12] J. Petřík and A. Kočan, *Chem. Listy*, 86 (1992) 694.
- [13] A. Pacáková-Kubátová, Diploma Thesis, Department of Analytical Chemistry, Charles University, Prague 1994.
- [14] B. Vrana, K. Dercová and Š. Baláz, *Biotechnology Techniques*, 9 (1995) 333.