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Enantiomer separation of polychlorinated biphenyl atropisomers and polychlorinated biphenyl retention behavior on modified cyclodextrin capillary gas chromatography columns

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Abstract

Seven commercially-available chiral capillary gas chromatography columns containing modified cyclodextrins were evaluated for their ability to separate enantiomers of the 19 stable chiral polychlorinated biphenyl (PCB) atropisomers, and for their ability to separate these enantiomers from achiral congeners, necessary for trace environmental analysis of chiral PCBs. The enantiomers of each of the 19 chiral PCBs were at least partially separated on one or more of these columns. Enantiomeric ratios of eleven atropisomers could also be quantified on six columns as they did not coelute with any other congener containing the same number of chlorine atoms, so could be quantified using gas chromatography–mass spectrometry. Analysis of a lake sediment heavily contaminated with PCBs showed enantioselective occurrence of PCB 91, proof positive of enantioselective in situ reductive dechlorination at the sampling site. Published by Elsevier Science B.V.

Keywords: Enantiomer separation; Retention behavior; Polychlorinated biphenyl atropisomers

1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous contaminants of great environmental concern. Although their use has been banned in most countries since the late 1970s, these compounds remain priority pollutants due to their persistence, toxicity, and bioaccumulation [1].

Of the 209 PCB congeners, 78 display axial chirality in their non-planar conformations (Fig. 1). Kaiser [2] predicted that of these atropisomers, as these conformational isomers are known, the 19 congeners with three or four *ortho* chlorine atoms exist as pairs of stable enantiomers at ambient temperatures as a result of restricted rotation about the central C–C biphenyl bond. This prediction was confirmed experimentally [3–5], with measured free energies of activation for racemization of >175 kJ/mol for tri-*ortho* atropisomers and ~250 kJ/mol for tetra-*ortho* atropisomers. These values are well above the energy barrier required for rotational stability at environmental temperatures (about 90 kJ/mol) and result in a half-life of $\geqslant 2\times 10^{11}$ *years* at 37°C for PCB 183, the most labile atropisomer studied [4]. With this high energy barrier to racemization, these 19 atropisomers are stable even under the elevated temperatures needed to separate their enantiomers via high resolution chiral gas chroma-

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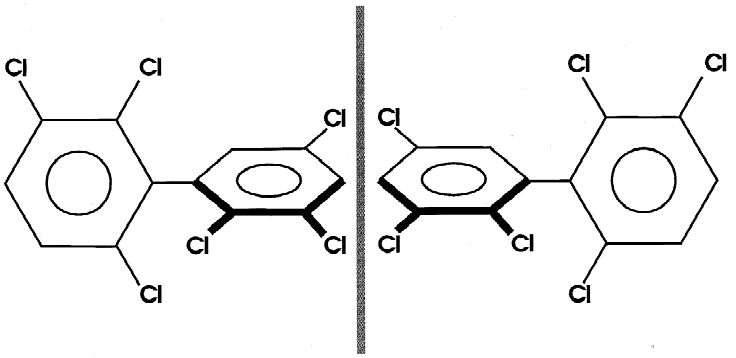

Fig. 1. Enantiomers of atropisomeric PCB 135 (2,2′,3,3′,5,6′-hexachlorobiphenyl).

tography (GC) [3–5]. At least half of these atropisomers are present in commercial PCB products (Aroclors, Clophens, Kanechlors, etc.) at ⩾1% by weight [6]. As a result, chiral PCBs are readily present in the environment. Although they were originally released as racemates, they may now be present enantioselectively due to metabolism and biological processing of these compounds by biota.

Quantification of the enantiomeric occurrence of chiral PCBs is important for several reasons. The enantiomers of chiral compounds have different biological and toxicological effects. Enantiomers of PCB atropisomers have different potencies in inducing cytochrome P450 activity (which metabolizes many xenobiotic compounds) and in accumulating uroporphyrin [7,8]. Chiral compounds can also be used as a tracer of biotic activity, and thus provide enhanced insights into environmental fate processes [9–16]. A number of studies [17–25] have reported the separation of PCB atropisomers using modified cyclodextrin GC columns, and initial work has been done to quantify enantiomeric ratios (ERs) of PCBs in environmental matrices, such as biota [22,25–28], sediment [29,30], and human milk [31]. However, the occurrence, distribution, and fate of chiral PCB atropisomers in the environment are still not well understood, as the analytical methodology for measuring chiral PCBs in complex environmental media is difficult. Investigators to date have used expensive and/or complicated instrumentation that is not commonly available, such as multidimensional gas chromatography (MDGC) [19,25,27–31], to measure ERs of PCB atropisomers in environmental samples.

In this paper, we report the separation of the enantiomers of all 19 stable PCB atropisomers by chiral capillary gas chromatography using commercially available modified cyclodextrin GC columns, and the separation of some of the atropisomers from interfering congeners and other environmental analytes that are usually present in a real environmental sample using benchtop gas chromatography–mass spectrometry (GC–MS).

2. Material and methods

PCB atropisomers were separated and quantified via high resolution chiral GC on a Hewlett-Packard 5890 gas chromatograph with electron capture detection (GC–ECD), and on a Hewlett-Packard 6890 gas chromatograph with an HP 5973 mass selective detector (GC–MS) using electron ionization (EI). A suite of modified cyclodextrin columns was evaluated: Chirasil–Dex (Chrompack, Raritan, NJ, USA; 25 m×0.25 mm internal diameter (I.D.)×0.25 μm film thickness (d_f)), with immobilized permethyl 2,3,6-tri-*O*-methyl β-cyclodextrin on a polysiloxane backbone as the stationary phase [32]; Cyclosil-B (J&W, Folsom, CA, USA; 30 m×0.32 mm I.D.× 0.25 μm d_f), with 30% 2,3-di-*O*-methyl-6-*O*-*tert.*-butyl dimethylsilyl β-cyclodextrin in DB-1701; B–PA Chiraldex (Astec, Whippany, NJ, USA; 30 m× 0.32 mm I.D.×0.25 μm d_f), with permethyl β-cyclodextrin; B–DM Chiraldex (Astec; 20 m×0.25 mm I.D.×0.25 μm d_f), with 2,3-di-*O*-methyl β-cyclodextrin; G–TA Chiraldex (Astec; 30 m×0.32 mm I.D.×0.125 μm d_f), with 2,6-di-*O*-pentyl-3-tri-

fluoroacetyl γ-cyclodextrin; B–PH Chiraldex (Astec; 30 m×0.32 mm I.D.×0.125 μm d_f), with (*S*)-2-hydroxypropyl methyl ester β-cyclodextrin; and G–PT Chiraldex (Astec; 12 m×0.25 mm I.D.×0.125 μm d_f), with hydroxypropyl–permethyltrifluroacetyl γ-cyclodextrin. Retention columns (Astec; 5 m×0.25 mm I.D.) were typically coupled before the chiral column.

GC conditions varied depending on the column used. For GC–ECD, 1 μl sample aliquots were splitless injected (injector 210°C, split opened after 0.7 min) at an oven temperature of 60°C with a 2 min hold, 10°C/min–150°C, 1°C/min to the column's maximum temperature (180–250°C), hold 20 min, with He carrier gas, under constant head pressure (1.65 bar for Chirasil–Dex, Cyclosil-B, B–DM, and G–PT; 0.90 bar for all others) and a detector temperature of 350°C. For G–TA, which has a maximum temperature of 180°C, the hold at maximum temperature was for 140 min in order to elute PCB 196. GC–MS EI full scan chromatograms and mass spectra were collected under splitless injection (injector 250°C) and the same temperature programs as with GC–ECD, using He carrier gas at 1.0 ml/min constant flow. The GC–MS transfer line was set at 280°C, ion source at 230°C (70 eV electron energy), and quadrupole at 150°C. Racemization of atropisomers within injector ports, detectors, and GC–MS transfer lines are negligible [4], and are negligible under all conditions within the column.

Six of the chiral columns were also evaluated for their ability to separate the atropisomers with solutions of individual pure racemic congeners (Accustandard, New Haven, CT, USA) in hexane, and for separating these enantiomers from all other PCB congeners using the methods of Frame [33], with nine solutions collectively containing all 209 PCB congeners (Accustandard, 10 μg/ml per congener in isooctane diluted to 1.67 μg/ml) to characterize the retention behavior of PCBs in the columns.

3. Results and discussion

3.1. Separation of PCB atropisomers

We have separated the enantiomers of all 19 stable PCB atropisomers by chiral GC, at least to some degree (Table 1). Several studies have reported the GC separation of atropisomers on a number of custom-made and commercially-available cyclodextrin chiral columns [17–26]. Hardt et al. [20] reported the separation of 15 of the 19 stable atropisomers, but using custom-made columns. To our knowledge, this is the first time the enantiomers of all 19 stable PCBs have been at least partially separated by chiral GC. Our results show that separation of PCB atropisomers is feasible using commercially available columns, which facilitates enantiomer analysis of these compounds since manufacturing GC columns by the analyst is a nontrivial procedure. Our chiral resolution values are comparable with previous results, such as that reported by Haglund and Wiberg [21] for Chirasil–Dex. Our reported resolution values could be optimized further by the use of shorter columns, which increase selectivity and improve resolution due to lower elution temperatures, at the expense of decreased efficiency.

Fig. 2 shows chromatograms of mixtures of all 19 atropisomeric PCBs on four columns (Chirasil–Dex, B–PA, B–DM, and Cyclosil-B) that appear promising for use in chiral PCB analysis, as they separate enantiomers of a number of congeners. Different columns separate different congeners, and to differing degrees. The mechanisms for GC enantiomer separation are not well understood, and there are currently no methods to predict separation capability a priori. Haglund and Wiberg [21] noted that Chirasil–Dex separated enantiomers of all PCBs that are 2,3,6-substituted in at least one ring except PCB 45, but did not separate enantiomers of congeners that have at least one ring 2,3,4,6-substituted and neither ring 2,3,6-substituted, suggesting that enantiomer recognition in Chirasil–Dex is strongly governed by 2,3,6-substitution. The same dependence was observed for HPLC separation of atropisomers on permethylated β-cyclodextrin [34]. However, the B–PA column, which contains the same type of chiral selector in the stationary phase (permethylated β-cyclodextrin), does *not* separate some 2,3,6-substituted atropisomers (PCBs 91, 95, 149) separated by Chirasil–Dex, and *does* partially separate some atropisomers (PCBs 131, 175) that are not separated by Chirasil–Dex. The reasons for these discrepancies are unknown, but may be due to

Table 1
Peak resolution (R[a]) of racemic PCB atropisomers on chiral GC columns[b] in this study

PCB atropisomer		Peak resolution (R)						
IUPAC no.	Substitution	B–PA	B–DM	G–TA	B–PH	G–PT	C–Dex	Csilb
45	236–2	–	1.7	1.1	–	–	–	1.6
84	236–23	1.2	–	0.8	–	–	0.7	–
88	2346–2	–	–	1.2	–	–	–	–
91	236–24	–	1.9	0.7	–	–	0.9	1.4
95	236–25	–	1.9	0.4	–	–	1.3	1.4
131	2346–23	0.6	0.6	1.0	–	0.5	–	–
132	234–236	1.1	–	0.8	0.7	–	1.5	–
135	235–236	1.2	–	0.7	–	–	0.8	–
136	236–236	0.9	1.4	–	0.6	1.0	0.8	1.0
139	2346–24	–	–	1.0	–	–	–	–
144	2346–25	0.5	–	–	–	–	–	–
149	236–245	–	1.0	1.0	–	0.4	1.3	0.6
171	2346–234	–	–	1.0	–	–	–	–
174	2345–236	1.3	–	0.7	–	–	0.8	–
175	2346–235	0.5	–	0.4	0.5	–	–	–
176	2346–236	0.6	0.9	–	–	1.2	0.8	0.6
183	2346–245	–	–	0.6	0.8	–	–	–
196	2345–2346	–	–	0.7	0.4	–	–	–
197	2346–2346	–	–	–	–	0.7	–	–

[a] R=(retention time$_{peak2}$−retention time$_{peak1}$)/0.5×(base width$_{peak2}$+base width$_{peak1}$). R=– indicates no separation of enantiomers.
[b] C–Dex=Chirasil–Dex; Csilb=Cyclosil-B; other abbreviations for columns defined in text.

differing amounts of the permethylated β-cyclodextrin chiral selector in the two columns. Another reason may be due to different achiral modifiers changing the chiral resolution. In Chirasil–Dex, the chiral selector is chemically bonded to the polysiloxane stationary phase backbone [32], whereas in B–PA, permethylated β-cyclodextrin is unbonded. As a result, chiral compounds may interact with the chiral selector in Chirasil–Dex, which has a fixed geometry, in a different manner than in B–PA. A third reason may be due to phase purity. Vetter et al. [35] found that a randomly modified *tert*.-butyldimethylsilylated cyclodextrin phase separated several pairs of organochlorine enantiomers that the pure phase could not. This could explain the discrepancy observed with the inability of our Cyclosil-B column to separate the enantiomers of PCB 132, which also cannot be separated using a pure phase of this chiral selector [35], while another column with the same selector in slightly greater proportions (35% 2,3-di-*O*-methyl-6-*O*-*tert*.-butyl dimethylsilyl β-cyclodextrin vs. 30%) separated this congener [22]. Differences observed in separations may be due to differing purities of the chiral selectors used for making both commercial and custom-made columns.

One concern with chiral GC analysis of PCB atropisomers is racemization due to heating at elevated temperatures. With the high rotational energy barrier [3–5], the amount of racemization is negligible for most chiral GC conditions. However, analysis times should not be extended for hours at high temperatures. The separation of PCB 196 by G–TA, the only column we studied that could even partially separate this congener for a reasonable measurement of ER (Table 1) took 2.5 h (retention time 158.2, 159.7 min); however, the maximum temperature of this column (180°C) will not racemize PCB 196 appreciably over this time period. Further research is needed to shorten the analysis time and optimize the separation of PCB 196 enantiomers.

3.2. Separation of PCB enantiomers from other congeners and interfering compounds

The other challenge in chiral GC analysis of PCB

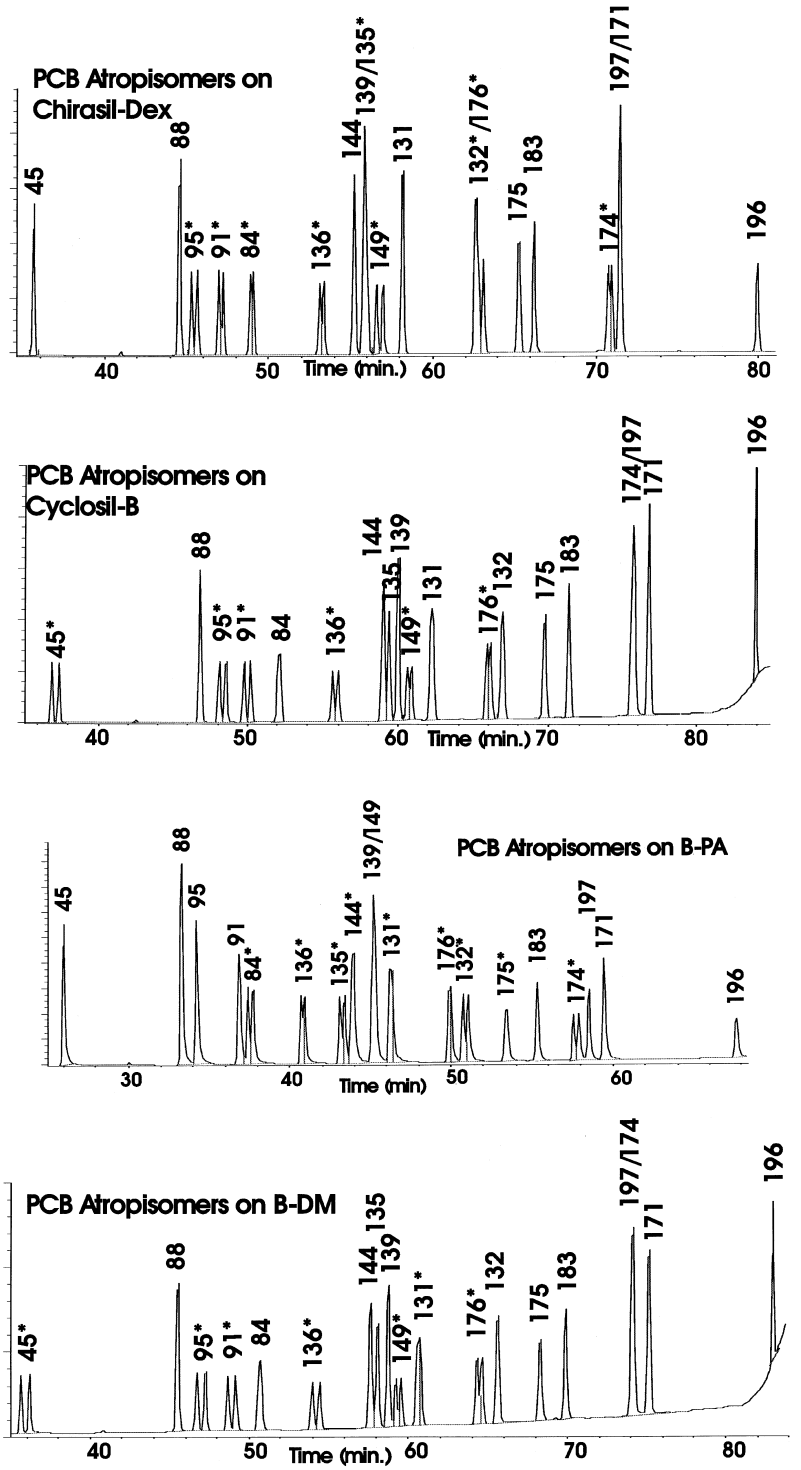

Fig. 2. GC–ECD chromatograms of the 19 racemic PCB atropisomers on Chirasil–Dex, Cyclosil-B, B–PA, and B–DM. Atropisomers with asterisks can be separated on the respective column (Table 1). Chromatographic conditions are given in text. Enantiomers of PCBs 132 and 176 are separated on Chirasil–Dex but coelute.

atropisomers is separating enantiomers from interfering peaks, especially other PCB congeners, as well as other hydrophobic compounds commonly found in environmental samples and present in extracted and cleaned-up samples (e.g., DDT, chlordane compounds, chlorobenzenes, etc.). The few published reports on PCB enantiomer analysis in real-world environmental samples have almost all used multidimensional GC (MDGC) [25,27–31]. Typically in MDGC, samples are injected into an achiral column, and selected fractions are cut after elution from the first column onto a second column (generally the chiral column). While MDGC is marketed commercially, it unfortunately is expensive and not commonly available. Recently, HPLC has been used as a preparative technique to fractionate PCBs depending on the level of *ortho* substitution [25,28], with subsequent chiral GC analysis of fractions containing atropisomers. This approach makes for a simpler chromatogram, but at the expense of more sample preparation. We wanted to investigate the feasibility of direct chiral PCB analysis on our chiral columns using typical benchtop equipment (e.g., GC–ECD, GC–MS) and minimizing the amount of chiral sample preparation needed, by characterizing the retention behavior of all 209 PCB congeners. The purpose of this analysis is not to use chiral columns for comprehensive congener-specific quantification, as there are a number of different achiral columns more suitable for that task [33], so no attempt was made to identify retention times of achiral congeners on the chiral columns. Rather, characterizing the retention behavior of PCBs on chiral columns would determine which atropisomers do not coelute with any other congener, thus allowing enantiomer analysis using GC–ECD for that column, or coelute only with congeners containing a different number of chlorines, for which enantiomer analysis can be done using GC–MS with selected ion monitoring (SIM).

Table 2 lists eleven atropisomers which satisfy the criteria listed above, and can be quantified directly on one or more of the the chiral GC columns we used for this part of the study (Chirasil–Dex, B–PA, B–DM, Cyclosil-B, B–PH, and G–TA). A number of atropisomers can be quantified on multiple columns (e.g., PCBs 91, 136, 149, and 176 on Chirasil–Dex, B–DM, and Cylosil-B), suggesting similarities between the different stationary phases in separating

Table 2
PCB atropisomers quantifiable on chiral GC columns in this study[a]

GC column	Atropisomers quantified
Chirasil–Dex	**91**, 136, 149, 174, 176
Cyclosil-B	91, 95, 136, 149, 176
B–PA	132, 144[b], **174**, 175[b], 176[b]
B–DM	**91**, 136, 149, 176[c]
B–PH	175[b], **183**
G–TA	**196**

[a] Chiral congeners do not coelute with any other PCB congener (bold), so can be quantified by GC–ECD, or coelute with congeners with different numbers of chlorine atoms, thus quantifiable using GC–MS under SIM.

[b] Enantiomers poorly separated on column.

[c] Heptachlorobiphenyl (PCB 182 or 192, neither of which are found in Aroclors [6]) coelutes with 176 on this column.

PCB congeners. We suggest that the analysis of chiral PCBs on columns whose retention behavior of PCBs has been characterized is an alternative analytical technique to the use of MDGC [25,27,28,30,31] and HPLC fractionation [25,28], with the advantages of simplicity and, at least with MDGC, less expense.

A number of caveats to this technique should be pointed out. There are few congeners that do not coelute with any other congener and are therefore suitable for GC–ECD: PCB 91 on Chirasil–Dex and B–DM, PCB 174 on B–PA, PCB 183 on B–PH, and PCB 196 on G–TA. Although trace environmental PCB analysis uses GC–ECD as a matter of choice due to its sensitivity, GC–ECD cannot distinguish between coelutions of congeners with different numbers of chlorine constituents, as GC–MS can, so GC–ECD is not often feasible for direct chiral PCB analysis. MDGC or HPLC fractionation would often be necessary if GC–ECD is used. In addition, other components in a sample extract may coelute with the PCB enantiomers in GC–ECD, which must be checked as required. On the other hand, our GC–MS analysis was done using the EI mode, which is not as sensitive as other GC–MS techniques (e.g., NCI, MS–MS) that can also be used for direct chiral GC analysis. In addition, although several atropisomers (e.g., PCBs 144, 175 and 176 on B–PA, and PCB 175 on B–PH) do not coelute with any other congener in their homologue series and can thus be quantified, the enantiomers of these congeners do not

separate particularly well, and therefore cannot make for a useful measurement. Finally, we recommend that direct chiral GC analysis should be preceded by characterizing retention behavior of each individual column using the methods of Frame [33]. This should be done even with columns of the same type we used, given the separation discrepancies reported with columns using the same chiral selector caused by phase impurities [35], differences in column dimension, and so forth. This retention behavior should also be monitored periodically as part of the quality assurance/quality control protocol for the chiral GC analysis, as some columns, such as the trifluoroacetylated cyclodextrin ones (G–TA, G–PT), may be prone to hydrolysis, and their retention behavior may change with time.

3.3. Application of analytical technique to environmental samples

Fig. 3 shows an example of the use of our PCB enantiomer analysis technique to measure ERs from an extract of a sediment from Lake Hartwell, SC, a manmade reservoir on the border between Georgia and South Carolina heavily impacted by PCBs from a capacitor plant spill into one of the tributaries to the lake. Sediment concentrations in Lake Hartwell are high, particularly within the Twelve Mile Creek arm, with total PCBs ranging from 10–150 μg/g and up in the mid-1980s [36,37]. Fig. 3 is the chromatogram trace of the enantiomers of PCB 91 in a sample of core G27. This core was taken in a survey of the lake in the mid-1980s [36,37] and is located at one of the highest concentrations of PCBs in the lake sediments. The sample shown in Fig. 3 was taken at the peak PCB concentration with depth in the core.

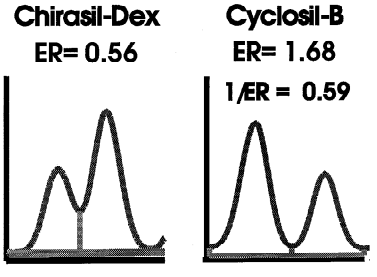

Fig. 3. PCB 91 enantiomers (Lake Hartwell sediment sample G27) on Chirasil–Dex and Cyclosil-B. Enantiomeric ratios are defined as concentration of first eluting enantiomer/concentration of second eluting enantiomer on each column. Elution order is reversed for PCB 91 in the two columns.

Clearly, PCB 91 is present in non-racemic quantities in this sample, with an ER (concentration of first eluting peak on Chirasil–Dex/concentration of second eluting peak) of 0.56. To date, there have only been a handful of measurements of PCB enantiomers in sediment. Glausch et al. [30] reported racemic levels of PCBs 95, 132, and 149 in Elsenz River sediment in southern Germany, while Benická et al. [29] reported non-racemic occurrence of PCB 95 in Standard Reference Material from the US National Institute of Standards and Technology taken from the Hudson River in New York State. A non-racemic ER is proof positive of biological processing of PCB 91, since abiotic processes would not affect the enantiomeric composition of a chiral compound. With the high concentration of PCBs present and the amount of time (years) that the sediments at the PCB peak level in G27 have been present in the lake bed, it is not surprising that reductive dechlorination of PCBs by sediment microorganisms has occurred. Earlier studies [36,37] found inconclusive evidence of reductive dechlorination within Lake Hartwell sediments based on shifts in congener profiles and accumulation of *ortho* only chlorinated PCB congeners, the end products of reductive dechlorination [38]. Thus, chiral analysis provides a simple way to show biotransformation of PCBs unequivocally.

It is also clear that the elution order of PCB 91 enantiomers is reversed between Chirasil–Dex and Cyclosil-B (Fig. 3). Reversal of elution order of enantiomers has been reported for other environmental chiral compounds on different columns, such as α-hexachlorocyclohexane [14], chiral chlordane constituents [15,39], and *o,p′*-DDT and *o,p′*-DDD [10]. As mentioned previously, the mechanisms for GC enantiomer separation are not well understood, and changes in elution sequence cannot be predicted.

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