Development of quantitative structure gas chromatographic relative retention time models on seven stationary phases for 209 polybrominated diphenyl ether congeners

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Abstract

Quantitative structure retention relationships (QSRRs) were developed to predict the gas chromatographic (GC) relative retention times (RRTs) for 209 polybrominated diphenyl ether (PBDE) congeners using the heuristic method included in the computer software Comprehensive Descriptors for Structural and Statistical Analysis (CODESSA). A total of 445 constitutional, topological, geometrical, electrostatic, and semi-empirical quantum chemical descriptors were derived for all PBDEs. Using experimental RRT data for 126 PBDE congeners from the literature, predictive regression models were built for seven individual GC capillary columns differing in stationary phases. Each model includes four descriptors which included Wiener index, Randic index, polarity parameter, etc., selected by CODESSA. High predictability was obtained. High multiple correlation coefficients R^2 indicated that >98.5% (except for stationary phase CP-Sil 19) of the total variation in the predicted RRTs is explained by the fitted models. The models were subsequently used to predict the RRTs of the remaining 83 PBDE congeners on seven different stationary phases. The statistical results show that, compared with others, DB-XLB column not only produces the least number of peak overlaps but also results in shorter retention times.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs), which have been manufactured in large quantities and widely used in a variety of consumer goods [1]. They spread ubiquitously as environmental contaminants and have been detected in a wide range of environmental samples and humans [2–5]. It is known that PBDEs are persistent, bioaccumulative, endocrine disrupting, and possibly carcinogenic [6].

Similar to polychlorinated biphenyls (PCBs), there are 209 possible PBDE congeners, differing in the number and positions of bromine atoms in the molecule. Unlike PCBs, however, only about a dozen congeners exist as major components in the commercial PBDEs mixtures [7]. Due to this fact and the lack of commercially available analytical standards, many previous PBDE studies have targeted on a limited number of congeners. However, a number of recent studies indicate that degradations of highly brominated PBDEs, such as the most heavily manufactured decabromodiphenyl ether, can lead to a variety of less brominated congeners [8,9]. The congener patterns of the degradation products are often complex, containing numerous congeners which may not exist in the PBDE technical mixtures. Accurate identification of these reaction products is essential in understanding the pathways and mechanisms of PBDE degra-

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dation processes, which determine their persistence and fate in the environment.

Analyses of PBDEs in environmental samples use high-resolution gas chromatography (HRGC) almost exclusively, coupled with appropriate detectors including electron-impact (EI) mass spectrometer (MS), electron-capture negative chemical ionization (NCI) MS or others [10–12]. Identification of the PBDE congeners in unknown samples relies on the matching of characteristic MS spectrum and/or the GC retention time with those of pure chemical standards. However, such efforts are often prohibited by the lack and/or the costs of the chemical standards. Predictive tools are needed to assist researchers in identifying PBDEs for which chemical standards are not available.

Quantitative structure retention relationships (QSRRs) describe the effects of an analyte's molecular structure on chromatographic retention time and also explore the mechanisms of absorption in stationary phase and elution from the column [13]. QSRRs have been developed for a number of halogenated organic contaminant groups [14–17]. For PBDEs, Rayne and Ikononou presented several predictive equations with five or seven simple parameters, including the numbers of *ortho*, *meta*, and *para* substituents, as well as molecular mass and calculated ionization potential and dipole moment, as independent variables [18–20]. The reliability of equations was examined by using basic statistics such as R^2 and F values rather than the predictions of relative retention times (RRTs) for PBDE congeners, which were not involved in model development. Also, their studies are limited to only one type of GC stationary phase (DB-5 or DB-5HT).

The purpose of this work was to characterize PBDE chromatographic retention properties on various stationary phases using topological and other molecular descriptors. A retention-time database obtained by Korytár et al. [21] was used to derive a series of QSRR models based on the heuristic method of Comprehensive Descriptors for Structural and Statistical Analysis (CODESSA) technique. The models were evaluated by predicting the GC-RRTs of PBDE congeners in a test set that was included in the database but independent of model development. Then, the experimental GC-RRTs of selected PBDEs (BDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) obtained in our laboratories are compared to the reference data and predicted values.

2. Methods

2.1. Chemicals and GC systems

Two sets of gas chromatographic (GC) retention times for PBDEs were obtained from our laboratories using different instruments and operational conditions. One of the analyses involved 14 PBDE congeners, including BDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209. The PBDE analytical standards were purchased from Cambridge Isotope Laboratory (Andover, MA). The analysis was performed on an Agilent 6890 GC coupled with a Waters Autospec Ultima high-resolution mass spectrometer (HRMS) (Waters Micro-mass, Manchester, UK) operating at 35 eV and the trap current

was 600 μ A. The GC was equipped with a CTC PAL autosampler. One microliter of sample was injected in splitless mode in a DB-5MS fused silica capillary column (12 m $\times$ 250 μ m i.d. $\times$ 0.25 μ m film thickness) with helium as carrier gas at a constant flow rate of 1.0 ml min⁻¹. The initial oven temperature was 110 °C, which lasted for 3 min. The oven temperature was increased to 285 °C at 15 °C min⁻¹, held for 4 min, and then increased to 325 °C at 10 °C min⁻¹, and held for 10 min.

The other laboratory work used nine PBDE congeners, including BDEs 28, 47, 66, 85, 99, 100, 153, 154, and 183. Separation was performed on an Agilent Model 6890 GC coupled with a Model 5973 low-resolution mass spectrometer (LRMS). Samples were introduced into the GC through a programmable temperature vaporization (PTV) large volume injection port. The temperature program for the PTV port was from 0 °C (held for 1.5 min) to 300 °C at 600 °C min⁻¹. A DB-5MS (30 m $\times$ 0.25 mm i.d., 0.25 μ m film thickness; J&W Scientific) capillary column was used for separation, with helium as the carrier gas at a flow rate of 1 ml min⁻¹. The initial oven temperature was 140 °C, which was held for 3 min, increased to 200 °C at 15 °C min⁻¹, increased to 220 °C at 2 °C min⁻¹, increased to 315 °C at 5 °C min⁻¹, and finally held for 5 min at 315 °C. The electron impact (EI) MS was operated in selected ion monitoring (SIM) mode.

2.2. Relative retention database for PBDEs

An experimental reference GC-RRT database was built by Korytár et al. [21]. The database contains RRTs for 126 PBDE congeners on seven GC columns of different stationary phases including DB-1 (100% dimethylpolysiloxane), DB-5 (5% phenyl 95% dimethyl arylene siloxane), HT-5 (5% phenyl siloxane-carborane), DB-17 (50% phenyl 50% dimethyl arylene siloxane), DB-XLB (proprietary phase), HT-8 (8% phenyl-polycarboranesiloxane), and CP-Sil 19 (14% cyanopropyl-phenyl, 86% dimethyl polysiloxane). All experiments were carried out with an Agilent 6890 GC equipped with an electron capture detector (ECD). The RRTs were calculated by dividing the obtained retention times by the sum of the retention times for 2,2',4,4'-tetrabrominated diphenyl ether (BDE47) and 2,2',3,4,4',5',6-heptabrominated diphenyl ether (BDE-183).

In this work, this reference database was divided into two parts. A total of 100 PBDE congeners in the database formed a "training set" for model development, and the other 26 congeners were used as a "test set". These 26 congeners were randomly chosen, with the number of bromines ranging from 2 to 8.

2.3. Model development using CODESSA

In this work, chemical structures of 209 individual PBDE congeners were drawn and modeled using the MM+ method of HyperChem Release 7.0 software (Hypercube, 2002). Optimization of the chemical structures was performed with the semiempirical AM1 method in HyperChem Release 7.0 software and saved as hin files for MOPAC [22]. Then, the hin files were transferred into CODESSA [23,24] software program to calculate a set of 445 constitutional, topological, geometrical,

electrostatic, and semi-empirical quantum chemical descriptors for each of the 209 PBDE congeners.

One of the computational procedures built in CODESSA uses the heuristic method. The advantages of the heuristic method are the high speed of computation and the absence of restrictions on the size of the data set. The heuristic method proceeds with a pre-selection of descriptors by sequential elimination of descriptors, which do not meet any of the following criteria: (i) the F -test greater than one unit; (ii) R^2 value less than a value defined at the start (default 0.01); (iii) the Student's t -test less than that defined (default 0.1); and (iv) duplicate descriptors having a higher squared inter-correlation coefficient than a predetermined level (usually 0.8).

The goodness of the correlation was examined by the correlation coefficient (R^2), the F -test (F), and the squared standard error (s^2). The stability of the models was evaluated against the cross-validated coefficient, R_{cv}^2 , which describes the stability of an obtained regression equation by focusing on the sensitivity of the model to the elimination of any single data point.

3. Results

By the heuristic method, regression equations were obtained using the GC-RRTs of the 100 BDE congeners in the training set for seven different stationary phases. The heuristic correlations performed provided the optimal equations for different numbers of descriptors in the range of 1–6. Plots of R^2 and R_{cv}^2 values against the number of descriptors (Fig. 1), which provided guidance in deciding the number of descriptors to be retained in the models, suggested that effectual models included four descriptors. The abbreviations of the descriptors are listed in Table 1 and the resulting regression equations for individual GC stationary phases are summarized in Table 2. The reference and predicted GC-RRT values for the training set on seven stationary phases are given in Table 3.

The multiple correlation coefficients (R^2) are higher than 0.985 for all GC stationary phases except CP-Sil 19 (Table 2). The overall F -values of >700 and the PRESS (predicted error

Fig. 1. Correlation coefficients (R^2 , R_{cv}^2) (seven models) vs. number of descriptors.

Table 1

The abbreviation of the descriptors' name

	Descriptor	Abbreviate
1	Wiener index ^a	W
2	Complementary information content (order 0) ^a	C
3	Maximum partial charge for a Br atom [Zefirov's PC] ^b	Max _{Br}
4	Minimum electrophilic reaction index for a O atom ^c	Min _O
5	Principal moment of inertia A ^d	PA
6	XY shadow/XY rectangle ^d	XY _{Shadow}
7	Randic index (order 3) ^a	R
8	RPCG relative positive charge (QMPOS/QTPLUS) [Zefirov's PC] ^b	RPCG
9	Min partial charge for a C atom [Zefirov's PC] ^b	Min _C
10	Polarity parameter ($Q_{\max} - Q_{\min}$) ^b	P
11	HOMO-1 energy ^c	HOMO-1
12	Moment of inertia C ^d	MC

^a Topological descriptor.

^b Electrostatic descriptor.

^c Quantum-chemical descriptor.

^d Geometrical descriptor.

sum of squares) of <0.00074 (except for CP-Sil 19, Table 3) demonstrate that the regressions are highly significant.

The results in Table 2 indicate that GC-RRTs of PBDEs on the four stationary phases DB-1, DB-5, HT-5, and DB-17 are strongly dependent on the Wiener index [25], the first topological index used in chemistry [26]. It is the sum of distances between all the pairs of vertices in a hydrogen-suppressed molecular graph. The coefficient of correlation between the GC-RRTs of PBDEs and Wiener index was 0.987, 0.989, 0.983, and 0.986, respectively, for the four stationary phases. GC-RRTs of PBDEs on the stationary phases DB-XLB, HT-8, and CP-Sil 19 are dependent strongly on the third order simple Randic index, an adjacency-based topological index proposed by Randic [27], with the correlation coefficients being 0.983, 0.982, and 0.891, respectively.

The RRTs of 26 BDE congeners in the test sets were obtained using the models presented in Table 2. Good predictive ability was demonstrated by the results, as shown in Fig. 2. For all stationary phases with the exception of CP-Sil 19, the regressions of predicted RRTs versus reference RRTs have slopes close to unity (0.995–1.104). R^2 ranges from 0.985 to 0.996 and is not statistically different from those reported in Table 2 for the training sets for each of the seven stationary phases.

4. Discussions

4.1. The major contributing molecular descriptors

The correlations between RRTs of organic compounds and Wiener index or Randic index (order 3) show that the magnitude of intermolecular interactions between the compounds and the stationary phase is related to the degree of branching of the molecules. For example, Wang et al. [28] showed that there were significant relationships between retention indices of saturated

Table 2
Regression equations on different stationary phases

	Intercept	W	C	MaxBr	Mino	PA	XY _{Shadow}	R	RPCG	MinC	P	HOMO-1	MC
DB-1	−1.029	1.34E−03	1.58E−02	6.878	−39.62								
DB-5	−5.42E−02	1.40E−03		6.318	−30.66	1.857							
HT-5	−1.205	1.41E−03	1.86E−02	7.748	−45.74								
DB-17	−1.008	1.32E−03	1.38E−02	7.681			0.237						
DB-XLB	−1.601							0.164	−3.082	2.764	6.18		
HT-8	−1.915							0.174	−1.078	2.917		−0.136	
CP-Sil 19	−9.409		0.131			−5.36		0.203					−79.99

esters on seven stationary phases of different polarity and the Wiener index or Randic index. For PBDEs as well as similarly structured polyhalogenated aromatics such as PCBs, it is not difficult to understand the relationships. The Wiener index that represents molecular “steric-branching” increases as the number of halogen substitution increases since it is defined as the half-sum of all topological distances in the hydrogen-depleted graph representing the skeleton of the molecule.

Within a PBDE homolog, the positions of bromines determine the optimal molecular conformation and affect the GC retention. The differences in RRTs among structural isomers may not be fully accounted for by either Wiener or Randic index alone although plots of reference RRTs [21] versus either of these indices alone result in positive slopes in most cases. It is noticed that Wiener index tends to increase with increasing number of *para* bromines and to decrease with increasing *ortho* bromines, within individual homologs. The Wiener index also tends to be lower if one of the two phenyl rings is fully brominated or if all bromines are on the same ring.

The descriptor “maximal partial charge for a Br atom [Zefirov’s PC]” reflects the characteristics of the charge distribution of a molecule; “minimum electrophilic reaction index for an oxygen atom” estimates the relative reactivity of the atoms in the molecule for a given series of compounds and are related to the activation energy of the corresponding chemical reaction. For PBDEs with similar structures, such as those having the same number of bromine, these factors will play important roles in deciding the elution order on columns.

4.2. Comparison between RRT prediction approaches

For halogenated aromatic compounds, various approaches of RRT prediction have been proposed. Ong and Hites [14] introduced linear predictive equations to investigate the relationships between three physical properties (molecular polarizabilities, ionization potentials, and dipole moments) and RTs of three groups of compounds (PAH, PCB, PCDF). They found molecular polarizability was the most important variable. Rayne et al. [20] reported a gas chromatographic relative time model, which uses molecular descriptors including the number of *ortho*-, *meta*-, and *para*-bromine substituents, the calculated dipole moment, and the natural logarithm of molecular weight, to predict GC retention times of the 163 individual PBDE congeners by using GC-RRTs of 46 available PBDEs on DB-5 stationary phase. The resulting model is:

$$\begin{aligned}
 \text{RRT} = & (-6.597 \pm 0.253) + (-0.076 \pm 0.007)(\text{no. } o\text{-Br}) \\
 & + (-0.041 \pm 0.007)(\text{no. } m\text{-Br}) \\
 & + (-0.021 \pm 0.011)(\text{no. } p\text{-Br}) + (0.012 \pm 0.006)(\mu) \\
 & + (1.247 \pm 0.046)(\ln \text{MW}), \\
 R^2 = & 0.997, \quad F = 1137.2, \quad n = 46
 \end{aligned} \quad (3)$$

An apparent advantage of this type of approach is the use of structural parameters that have straightforward physical meanings and are familiar to most analytical chemists. Our study, to our knowledge, is the first one using combinations of con-

Table 3
Elution order of 100 BDE congeners (training set), 26 BDE congeners (test set) and predicted set (83 BDE congeners) on seven capillary columns and their ref. [21] and predicted GC-RRT

DB-1			DB-5			HT-5			DB-17			DB-XLB			HT-8			CP-Sil 19		
BDE	PRE	REF	BDE	PRE	REF	BDE	PRE	REF	BDE	PRE	REF	BDE	PRE	REF	BDE	PRE	REF	BDE	PRE	REF
1	0.082	0.100	1	0.034	0.095	2	0.046	0.091	2	0.039	0.086	1	0.035	0.086	1	0.039	0.084	1	0.106	0.083
2	0.062	0.102	2	0.068	0.097	1	0.070	0.091	1	0.071	0.087	2	0.032	0.088	2	0.028	0.085	2	0.128	0.083
3	0.056	0.103	3	0.109	0.099	3	0.039	0.093	3	0.049	0.088	3	0.057	0.090	3	0.061	0.087	3	0.033	0.086
<i>a</i> 10	0.136	0.125	10	0.100	0.123	10	0.123	0.112	14	0.102	0.114	10	0.090	0.117	10	0.104	0.116	54	0.098	
9	0.130	0.131	9	0.095	0.129	9	0.116	0.116	9	0.114	0.117	9	0.108	0.123	9	0.102	0.122	10	0.145	0.116
14	0.127	0.133	14	0.092	0.130	14	0.111	0.117	10	0.122	0.117	14	0.098	0.124	14	0.090	0.124	14	0.182	0.118
7	0.124	0.134	7	0.105	0.133	7	0.108	0.121	7	0.130	0.122	4	0.137	0.127	7	0.124	0.129	9	0.214	0.120
4	0.130	0.134	4	0.101	0.133	6	0.126	0.121	11	0.116	0.124	7	0.114	0.128	6	0.129	0.130	7	0.200	0.125
6	0.139	0.135	6	0.119	0.134	4	0.116	0.122	6	0.127	0.125	6	0.119	0.128	4	0.144	0.131	6	0.196	0.127
11	0.118	0.139	11	0.116	0.137	11	0.102	0.124	13	0.101	0.129	11	0.119	0.133	11	0.120	0.134	11	0.200	0.130
8	0.150	0.139	8	0.144	0.139	8	0.137	0.126	8	0.130	0.129	8	0.129	0.135	8	0.138	0.137	4	0.118	0.130
13	0.128	0.142	12	0.129	0.142	13	0.111	0.128	12	0.164	0.129	12	0.162	0.138	12	0.160	0.139	8	0.224	0.134
12	0.132	0.142	13	0.176	0.142	12	0.116	0.128	4	0.128	0.129	5	0.139		13	0.135	0.140	12	0.196	0.135
15	0.133	0.146	15	0.194	0.147	30	0.126	0.152	15	0.121	0.133	13	0.130	0.140	5	0.147		13	0.098	0.136
30	0.148	0.172	5	0.154		27	0.191	0.162	5	0.161		15	0.175	0.147	15	0.178	0.147	15	0.094	0.142
5	0.172		30	0.153	0.174	5	0.163		30	0.204	0.166	30	0.174	0.174	30	0.180	0.175	5	0.166	
27	0.203	0.180	27	0.193	0.184	19	0.159	0.168	36	0.184	0.177	27	0.184	0.184	27	0.190	0.188	30	0.164	0.167
19	0.175	0.181	19	0.169	0.187	18	0.186	0.169	34	0.195	0.179	19	0.196	0.186	34	0.192	0.196	27	0.207	0.185
18	0.199	0.186	18	0.191	0.191	34	0.192	0.169	26	0.189	0.184	18	0.208	0.192	19	0.205	0.196	34	0.196	0.189
34	0.205	0.188	34	0.193	0.192	26	0.191	0.172	27	0.189	0.184	34	0.186	0.196	18	0.209	0.196	19	0.028	0.193
26	0.205	0.190	26	0.196	0.195	29	0.181	0.173	29	0.204	0.186	26	0.196	0.198	23	0.199		18	0.209	0.193
32	0.210	0.190	32	0.204	0.195	32	0.197	0.175	18	0.189	0.188	29	0.239	0.198	26	0.193	0.200	29	0.221	0.193
29	0.196	0.193	29	0.191	0.197	36	0.186	0.178	39	0.187	0.189	32	0.197	0.199	29	0.230	0.202	36	0.195	0.194
36	0.201	0.196	36	0.193	0.199	25	0.204	0.182	32	0.205	0.191	36	0.179	0.203	32	0.220	0.205	26	0.232	0.194
17	0.209	0.196	17	0.209	0.202	31	0.205	0.182	19	0.194	0.194	17	0.213	0.205	36	0.181	0.206	32	0.242	0.197
25	0.217	0.198	25	0.223	0.204	17	0.197	0.183	31	0.200	0.195	25	0.200	0.208	25	0.212	0.213	25	0.207	0.204
31	0.218	0.199	31	0.209	0.205	39	0.198	0.186	25	0.202	0.195	31	0.228	0.212	31	0.232	0.213	39	0.214	0.205
39	0.212	0.203	39	0.208	0.208	33	0.187	0.193	17	0.198	0.199	39	0.213	0.215	17	0.222	0.214	17	0.203	0.206
33	0.202	0.207	33	0.206	0.214	38	0.200	0.193	38	0.247	0.204	23	0.217		39	0.221	0.217	31	0.263	0.206
28	0.217	0.207	28	0.219	0.214	16	0.228	0.193	28	0.224	0.206	16	0.243	0.218	24	0.220		24	0.208	
16	0.236	0.207	16	0.234	0.214	15	0.116	0.193	35	0.222	0.209	33	0.256	0.218	38	0.247	0.226	23	0.210	
38	0.214	0.212	38	0.213	0.217	28	0.203	0.194	16	0.235	0.209	38	0.259	0.220	16	0.250	0.226	38	0.224	0.214
21	0.214		21	0.217		21	0.200		20	0.246	0.209	24	0.221		33	0.263	0.226	28	0.264	0.216
20	0.247	0.214	35	0.238	0.221	35	0.211	0.201	33	0.214	0.210	28	0.233	0.223	28	0.240	0.227	16	0.199	0.217
35	0.224	0.215	20	0.251	0.221	20	0.240	0.201	22	0.243	0.221	35	0.247	0.228	35	0.248	0.235	33	0.254	0.218

Table 3 (Continued)

22	0.259 0.223	23 0.225	22	0.252 0.211	37	0.246 0.221	20	0.230 0.228	20	0.233 0.235	20	0.222 0.223	
37	0.243 0.223		37	0.233 0.211	23 0.225	22	0.245 0.242	22	0.253 0.247	35	0.233 0.224		
24 0.235		22	0.279 0.231	54 0.226	24 0.226	37	0.280 0.242	37	0.281 0.247	22	0.228 0.235		
54 0.241	37	0.265 0.232	24 0.227	80 0.289 0.255		21 0.267	21 0.266		37	0.240 0.236			
23 0.242	54 0.250		53	0.250 0.232	21 0.259	53	0.289 0.268	53	0.308 0.272	21 0.240			
53	0.263 0.253	53	0.266 0.264	73	0.273 0.234	72	0.282 0.261	73	0.260 0.269	73	0.258 0.273	45 0.254	
73	0.284 0.257	73	0.288 0.266	23 0.235	73	0.302 0.262	69	0.261 0.274	69	0.254 0.278	61 0.256		
69	0.262 0.258	69	0.281 0.268	69	0.247 0.238	69	0.301 0.265	50	0.274 0.278	50	0.283 0.287	73	0.216 0.264
50	0.279 0.261	50	0.288 0.272	50	0.268 0.247	54 0.274	72	0.287 0.289	72	0.283 0.291	69	0.227 0.264	
72 0.293 0.274		72 0.297 0.281		72 0.282 0.253		53	0.277 0.275	54 0.290	57 0.296	52 0.268			
62	0.331 0.277	52 0.284		62	0.327 0.256	50	0.297 0.278	51	0.290 0.296	62	0.329 0.297	53	0.255 0.269
51	0.271 0.278	62	0.332 0.287	80	0.273 0.267	68	0.302 0.280	75	0.293 0.296	80	0.287 0.304	50	0.229 0.272
75	0.289 0.278	51	0.278 0.289	49	0.307 0.269	49	0.302 0.290	62	0.340 0.296	68	0.292 0.308	57 0.273	
49	0.314 0.283	80	0.291 0.289	68	0.284 0.270	62	0.327 0.291	80	0.285 0.299	49	0.324 0.309	43 0.274	
52 0.283		75	0.307 0.290	51	0.258 0.271	67	0.298 0.294	57 0.302	59 0.310		59 0.276		
80	0.286 0.284	68	0.306 0.294	75	0.277 0.271	51	0.268 0.296	48	0.335 0.304	75	0.304 0.311	72	0.223 0.277
68	0.296 0.285	49	0.314 0.294	52 0.271	75	0.309 0.296	68	0.291 0.305	51	0.325 0.311	80	0.150 0.281	
71	0.280 0.287	48	0.301 0.298	48	0.280 0.272	52 0.296	49	0.318 0.305	48	0.332 0.313	62	0.256 0.283	
46	0.282 0.287	71	0.291 0.299	71	0.268 0.275	48	0.297 0.298	46	0.328 0.306	46	0.337 0.315	68	0.231 0.290
48	0.291 0.287	46	0.291 0.299	46	0.271 0.275	79	0.321 0.302	71	0.329 0.306	71	0.348 0.315	65 0.293	
67	0.300 0.294	67	0.312 0.303	67	0.289 0.279	58	0.328 0.302	59 0.310	54 0.315		51	0.203 0.296	
47 0.325 0.301		47 0.332 0.313		47	0.318 0.297	71	0.269 0.306	67	0.322 0.312	67	0.322 0.318	75	0.253 0.296
74	0.318 0.309	74	0.328 0.319	74	0.309 0.299	46	0.288 0.306	43 0.315	65 0.322		49	0.280 0.296	
76	0.306 0.311	45 0.319	76	0.296 0.300	70 0.307	52 0.317	43 0.324		48	0.288 0.298			
79	0.327 0.312	44 0.319	79	0.320 0.304	65 0.308	45 0.323		63 0.328	67	0.283 0.301			
58	0.338 0.312	79	0.334 0.321	58	0.333 0.304	47	0.315 0.308	47	0.322 0.326	61 0.329	63 0.302		
66	0.335 0.316	58	0.340 0.321	70 0.311	44 0.310	76 0.357 0.329		52 0.330	71	0.270 0.303			
42	0.334 0.317	43 0.322	44 0.312	45 0.311	74	0.356 0.334	45 0.335	46	0.246 0.304				
44 0.319	76	0.317 0.322	66	0.328 0.313	59 0.311	44 0.334	47	0.340 0.335	47	0.275 0.315			
70 0.319	70	0.323	42	0.329 0.313	78	0.340 0.322	79	0.339 0.335	74	0.351 0.338	70	0.317	
45 0.321	65	0.326	41	0.314	76	0.329 0.322	63 0.335	76	0.350 0.339	41	0.317		
41 0.321	66	0.346 0.328	45 0.316	66	0.322 0.326	58	0.303 0.335	79	0.348 0.341	44	0.317		
43 0.324	42	0.348 0.329	78	0.319 0.318	42	0.317 0.327	65 0.337	58	0.302 0.341	74	0.317 0.318		
78	0.327 0.325	61	0.332	43 0.318	61	0.327	61	0.340	42	0.345 0.350	64	0.318	
55	0.333 0.328	41	0.333	55	0.327 0.326	63	0.329	64	0.341	66	0.372 0.350	58	0.271 0.319
65 0.331	78	0.340 0.334	61	0.326	74	0.309 0.330	42	0.335 0.343	78	0.331 0.354	79	0.268 0.320	
61 0.331	59	0.334	65	0.327	43	0.334	66	0.361 0.343	64	0.354	76	0.312 0.322	
59 0.333	57 0.337		59	0.329	57	0.337	78 0.343 0.346		70	0.357	96	0.325	
57 0.336	55 0.351 0.341		57	0.332	56	0.338	55 0.354 0.356		44	0.359	56	0.327	

Table 3 (Continued)

81 0.350 0.339	64 0.349	81 0.345 0.335	64 0.342	70 0.357	55 0.349 0.363	111 0.331
64 0.342	81 0.363 0.350	103 0.390 0.336	41 0.342	81 0.377 0.365	41 0.370	42 0.287 0.332
77 0.341 0.343	63 0.353	64 0.338	81 0.355 0.344	41 0.367	81 0.367 0.370	66 0.307 0.332
40 0.325 0.344	40 0.340 0.355	60 0.338	55 0.348 0.349	40 0.373 0.372	103 0.372 0.373	78 0.300 0.333
60 0.344	77 0.360 0.355	121 0.386 0.339	77 0.349 0.350	77 0.409 0.372	121 0.364 0.375	55 0.308 0.347
56 0.346	60 0.358	56 0.341	40 0.335 0.351	104 0.363 0.373	56 0.377	81 0.319 0.349
63 0.352	56 0.363	104 0.348 0.344	121 0.419 0.362	56 0.373	40 0.385 0.380	121 0.292 0.356
104 0.358 0.357	104 0.376 0.369	40 0.320 0.347	60 0.364	103 0.383 0.374	77 0.412 0.380	60 0.358
103 0.396 0.358	103 0.407 0.369	77 0.334 0.347	103 0.413 0.372	121 0.374 0.377	104 0.378 0.382	104 0.273 0.359
121 0.393 0.363	121 0.409 0.371	63 0.348	104 0.390 0.383	60 0.386	60 0.391	77 0.329 0.359
102 0.374 0.385	102 0.393 0.396	102 0.366 0.370	120 0.409 0.394	102 0.418 0.396	94 0.397	113 0.359
100 0.413 0.395	100 0.427 0.405	101 0.412 0.389	101 0.408 0.403	94 0.400	102 0.423 0.404	40 0.307 0.360
101 0.416 0.401	101 0.424 0.410	109 0.433 0.395	100 0.414 0.403	111 0.412	111 0.405	103 0.338 0.360
119 0.417 0.405	120 0.432 0.414	100 0.409 0.396	102 0.414 0.408	100 0.385 0.413	113 0.408	94 0.373
98 0.398 0.405	119 0.435 0.414	120 0.416 0.398	98 0.394 0.414	96 0.413	112 0.409	92 0.376
109 0.434 0.406	98 0.416 0.414	119 0.412 0.400	119 0.425 0.416	113 0.414	92 0.417	90 0.385
120 0.420 0.408	109 0.446 0.417	98 0.392 0.400	93 0.418	101 0.439 0.418	101 0.436 0.418	102 0.343 0.389
88 0.428 0.411	96 0.419	125 0.404 0.403	92 0.419	92 0.421	100 0.393 0.424	100 0.341 0.394
96 0.411	88 0.437 0.423	91 0.408	96 0.419	112 0.422	120 0.433 0.424	91 0.397
91 0.412	125 0.422 0.424	88 0.428 0.409	95 0.422	119 0.429 0.423	96 0.424	95 0.399
125 0.409 0.414	89 0.426	96 0.409	109 0.456 0.427	120 0.430 0.423	109 0.414 0.425	120 0.346 0.400
89 0.414	91 0.429	89 0.411	99 0.421 0.430	98 0.402 0.423	119 0.432 0.428	101 0.395 0.400
82 0.423	94 0.430	82 0.420	91 0.430	90 0.424	98 0.399 0.428	119 0.376 0.403
122 0.424	99 0.432 0.433	122 0.421	127 0.465 0.430	125 0.441 0.426	125 0.444 0.431	98 0.359 0.403
99 0.419 0.425	93 0.433	99 0.414 0.424	90 0.433	109 0.425 0.427	91 0.433	109 0.403 0.407
84 0.427	84 0.437	116 0.450 0.424	124 0.447 0.435	88 0.438 0.431	95 0.434	112 0.410
94 0.427	95 0.438	84 0.427	94 0.435	95 0.434	88 0.439 0.438	125 0.409 0.415
93 0.431	115 0.470 0.442	94 0.428	125 0.440 0.436	93 0.435	90 0.438	88 0.393 0.416
95 0.433	124 0.459 0.443	124 0.453 0.432	122 0.437	91 0.436	93 0.441	93 0.419
116 0.447 0.434	92 0.443	93 0.433	84 0.440	83 0.441	83 0.443	83 0.419
115 0.460 0.434	122 0.443	95 0.434	83 0.441	99 0.441 0.443	99 0.451 0.447	107 0.420
124 0.452 0.436	83 0.443	115 0.462 0.435	112 0.443	124 0.462 0.453	116 0.476 0.452	99 0.400 0.422
83 0.436	116 0.449 0.444	83 0.436	113 0.443	84 0.453	124 0.455 0.454	116 0.454 0.430
113 0.438	82 0.444	113 0.438	89 0.443	116 0.488 0.454	84 0.455	115 0.410 0.430
92 0.439	113 0.444	92 0.440	88 0.424 0.444	89 0.455	117 0.456	124 0.411 0.432
112 0.445	112 0.448	111 0.446	115 0.446 0.445	117 0.455	115 0.462 0.458	84 0.432
111 0.445	111 0.451	90 0.446	117 0.447	115 0.457 0.457	107 0.461	89 0.438
90 0.446	90 0.452	112 0.446	111 0.448	127 0.452 0.465	89 0.463	127 0.359 0.439
127 0.438 0.449	127 0.453 0.454	110 0.451	82 0.448	86 0.478 0.466	127 0.443 0.469	117 0.441

Table 3 (Continued)

97	0.427 0.450	97	0.443 0.457	127	0.435 0.453	107	0.451	107	0.467	97	0.465 0.472	97	0.432 0.446
118	0.430 0.450	118	0.447 0.457	97	0.425 0.455	110	0.451	97	0.459 0.469	118	0.483 0.472	110	0.446
87	0.453 0.450	87	0.460 0.460	118	0.427 0.455	97	0.423 0.452	118	0.485 0.469	108	0.460 0.474	118	0.433 0.447
110	0.450	110	0.460	86	0.434 0.455	118	0.432 0.452	123	0.464 0.471	86	0.479 0.475	123	0.415 0.449
108	0.456 0.451	108	0.466 0.461	108	0.457 0.456	108	0.473 0.460	108	0.456 0.473	123	0.469 0.476	108	0.399 0.450
86	0.434 0.452	86	0.444 0.462	87	0.455 0.457	123	0.453 0.462	87	0.475 0.473	87	0.476 0.476	86	0.450 0.453
123	0.465 0.453	123	0.475 0.462	123	0.467 0.459	116	0.442 0.463	106	0.464 0.477	122	0.476	122	0.454
117	0.460	117	0.463	117	0.463	87	0.464 0.471	110	0.480	106	0.456 0.481	87	0.445 0.456
106	0.447 0.463	106	0.458 0.469	106	0.447 0.464	106	0.457 0.472	122	0.481	110	0.488	106	0.439 0.457
107	0.463	107	0.470	107	0.464	86	0.446 0.478	155	0.486 0.494	155	0.501 0.497	155	0.436 0.462
85	0.445 0.476	85	0.459 0.486	155	0.510 0.483	126	0.472 0.489	82	0.494	82	0.499	82	0.473
114	0.462 0.483	114	0.474 0.491	114	0.464 0.494	114	0.460 0.495	85	0.477 0.499	114	0.488 0.505	114	0.466 0.478
126	0.475 0.490	126	0.489 0.495	85	0.444 0.498	85	0.467 0.500	114	0.497 0.503	85	0.491 0.508	85	0.450 0.479
155	0.510 0.491	155	0.525 0.496	154	0.547 0.504	156	0.599 0.500	126	0.507 0.508	126	0.498 0.513	126	0.445 0.485
105	0.476 0.496	105	0.492 0.506	126	0.477 0.507	155	0.529 0.518	154	0.539 0.513	154	0.520 0.513	154	0.527 0.487
154	0.543 0.513	154	0.554 0.517	144	0.567 0.516	154	0.541 0.518	150	0.516	165	0.518	105	0.474 0.500
144	0.560 0.528	144	0.565 0.531	105	0.478 0.519	105	0.483 0.519	105	0.521 0.519	105	0.525 0.524	161	0.532 0.505
136	0.530	161	0.581 0.535	161	0.582 0.521	152	0.519	148	0.522	144	0.559 0.524	150	0.506
145	0.532	136	0.539	136	0.535	134	0.528	152	0.523	150	0.524	144	0.583 0.507
161	0.574 0.533	145	0.542	145	0.537	166	0.585 0.534	145	0.525	161	0.519 0.526	168	0.544 0.515
150	0.534	150	0.545	150	0.539	136	0.537	144	0.544 0.533	152	0.527	148	0.515
151	0.545	152	0.547	168	0.578 0.543	150	0.542	165	0.533	151	0.529	153	0.585 0.531
152	0.546	168	0.581 0.548	151	0.552	153	0.547 0.543	161	0.535 0.536	145	0.534	165	0.534
168	0.571 0.547	151	0.549	164	0.553	151	0.543	151	0.543	148	0.539	152	0.535
164	0.549	135	0.555	152	0.554	147	0.550	168	0.562 0.545	168	0.562 0.543	145	0.537
130	0.551	153	0.571 0.560	130	0.556	148	0.550	147	0.545	135	0.548	133	0.550
135	0.551	134	0.562	135	0.559	138	0.591 0.551	135	0.552	134	0.554	139	0.581 0.551
134	0.559	130	0.564	153	0.570 0.564	146	0.551	133	0.557	147	0.555	131	0.621 0.562
153	0.564 0.563	164	0.564	134	0.567	149	0.559	153	0.596 0.560	153	0.599 0.558	147	0.562
132	0.564	133	0.567	132	0.572	135	0.562	134	0.562	133	0.559	141	0.615 0.563
133	0.565	148	0.568	129	0.572	145	0.562	143	0.562	149	0.574	158	0.619 0.563
129	0.565	132	0.571	133	0.573	132	0.566	136	0.568	141	0.574 0.582	159	0.565 0.564
148	0.565	143	0.571	148	0.573	133	0.567	149	0.569	136	0.582	140	0.560 0.565
143	0.568	146	0.574	146	0.576	164	0.568	146	0.573	164	0.582	160	0.621 0.567
146	0.569	165	0.575	143	0.577	143	0.571	139	0.546 0.579	143	0.583	136	0.568
149	0.569	129	0.575	149	0.577	129	0.574	137	0.584	163	0.583	146	0.570
165	0.573	149	0.575	165	0.583	162	0.575	141	0.581 0.586	139	0.554 0.584	167	0.597 0.572
147	0.575	147	0.576	147	0.584	130	0.579	163	0.588	137	0.584	142	0.647 0.578
139	0.568 0.576	139	0.578 0.577	160	0.593 0.592	137	0.586	140	0.556 0.588	160	0.560 0.584	135	0.579

Table 3 (Continued)

131	0.558 0.586	141	0.574 0.585	141	0.577 0.594	142	0.567 0.588	131	0.563 0.590	131	0.556 0.586	151	0.581
137	0.586	131	0.568 0.586	139	0.575 0.595	168	0.569 0.588	158	0.590 0.590	158	0.594 0.586	162	0.583
163	0.586	158	0.598 0.587	137	0.595	165	0.589	159	0.572 0.591	159	0.566 0.587	149	0.593
140	0.564 0.586	140	0.573 0.588	163	0.596	131	0.574 0.595	130	0.592	146	0.589	166	0.660 0.603
158	0.587 0.586	159	0.587 0.590	162	0.597	163	0.596	164	0.592	162	0.592	138	0.636 0.605
141	0.569 0.587	160	0.585 0.590	131	0.565 0.598	159	0.594 0.597	160	0.572 0.592	167	0.615 0.594	164	0.607
162	0.588	163	0.591	169	0.598	158	0.598 0.597	167	0.619 0.596	140	0.580 0.597	169	0.610
160	0.582 0.589	162	0.593	158	0.596 0.598	141	0.581 0.603	162	0.596	142	0.570 0.599	143	0.613
169	0.591	137	0.593	159	0.588 0.603	140	0.548 0.603	142	0.585 0.597	130	0.602	134	0.615
159	0.580 0.593	167	0.587 0.596	142	0.576 0.610	169	0.605	129	0.601	129	0.602	130	0.617
142	0.566 0.595	142	0.568 0.598	167	0.580 0.613	157	0.606	132	0.607	132	0.619	137	0.619
167	0.575 0.600	169	0.604	140	0.571 0.614	161	0.600 0.609	138	0.609 0.619	138	0.615 0.620	163	0.624
157	0.605	157	0.613	157	0.615	160	0.555 0.609	166	0.605 0.627	166	0.610 0.622	184	0.759 0.636
138	0.593 0.618	138	0.600 0.617	175	0.639	144	0.584 0.624	157	0.632	169	0.637	156	0.654 0.637
166	0.598 0.623	166	0.601 0.621	166	0.610 0.643	139	0.581 0.626	169	0.641	157	0.639	175	0.646
175	0.634	156	0.606 0.640	138	0.603 0.644	167	0.576 0.631	156	0.627 0.642	156	0.620 0.640	132	0.646
156	0.597 0.644	184	0.694 0.666	156	0.606 0.672	175	0.650	188	0.645	188	0.648	157	0.651
184	0.695 0.673	128	0.585 0.677	184	0.710 0.683	179	0.655	184	0.645 0.654	184	0.653 0.652	129	0.659
176	0.676	176	0.678	176	0.690	188	0.672	186	0.671	183	0.702 0.665	183	0.843 0.685
128	0.573 0.679	179	0.682	183	0.742 0.703	184	0.689 0.679	183	0.703 0.674	178	0.667	182	0.825 0.696
179	0.689	183	0.721 0.687	179	0.706	186	0.681	179	0.674	182	0.684 0.675	128	0.686 0.704
183	0.724 0.699	186	0.691	185	0.736 0.716	183	0.730 0.692	176	0.675	185	0.678 0.676	192	0.828 0.722
186	0.700	178	0.694	182	0.748 0.717	171	0.697	128	0.647 0.680	192	0.665 0.678	185	0.856 0.722
178	0.703	188	0.696	186	0.719	176	0.700	178	0.680	186	0.678	191	0.859 0.746
188	0.704	182	0.723 0.697	192	0.753 0.720	128	0.604 0.702	182	0.680 0.680	179	0.679	188	0.761
182	0.729 0.707	175	0.698	178	0.720	187	0.702	175	0.693	128	0.672 0.682	181	0.885 0.823
171	0.713	185	0.709 0.702	188	0.722	182	0.720 0.708	185	0.690 0.693	175	0.682	178	0.829
185	0.716 0.713	192	0.724 0.707	171	0.729	174	0.709	192	0.680 0.698	176	0.685	179	0.833
174	0.715	174	0.708	128	0.580 0.730	192	0.741 0.710	187	0.703	191	0.726 0.695	176	0.833
177	0.716	177	0.708	174	0.733	185	0.690 0.714	191	0.727 0.708	187	0.712	187	0.849
187	0.718	187	0.710	177	0.734	178	0.715	174	0.711	172	0.716	173	0.927 0.850
170	0.720	171	0.712	170	0.736	172	0.718	177	0.715	174	0.718	186	0.850
172	0.720	172	0.715	187	0.737	180	0.728	172	0.715	177	0.720	190	0.919 0.852
192	0.732 0.721	170	0.720	172	0.738	191	0.746 0.729	171	0.715	193	0.722	172	0.862
193	0.729	191	0.728 0.721	191	0.745 0.744	177	0.730	193	0.726	171	0.723	193	0.862
191	0.728 0.734	193	0.722	193	0.748	193	0.732	180	0.737	180	0.737	171	0.878
180	0.742	180	0.736	180	0.761	170	0.738	181	0.692 0.744	190	0.739 0.742	180	0.878
189	0.749	189	0.746	189	0.768	189	0.746	170	0.750	181	0.708 0.742	189	0.893
181	0.733 0.770	181	0.725 0.754	173	0.734 0.807	181	0.730 0.761	173	0.709 0.755	173	0.698 0.743	174	0.893

Table 3 (Continued)

173 0.715 0.779	173 0.708 0.763	190 0.768 0.807	173 0.708 0.776	190 0.735 0.755	189 0.759	177 0.901
190 0.747 0.780	190 0.741 0.763	181 0.754 0.807	190 0.746 0.778	189 0.761	170 0.764	170 0.933
202 0.848	202 0.819	202 0.877	202 0.830	202 0.809	204 0.800 0.801	204 1.154 0.981
197 0.855	204 0.852 0.834	197 0.881	201 0.840	204 0.789 0.810	198 0.828 0.809	198 1.213 1.094
204 0.880 0.858	197 0.835	204 0.911 0.885	204 0.852 0.849	201 0.810	203 0.841 0.812	203 1.230 1.100
200 0.865	200 0.836	200 0.896	203 0.887 0.859	197 0.811	201 0.821	202 1.164
201 0.867	201 0.839	201 0.896	198 0.880 0.860	200 0.819	202 0.823	201 1.172
196 0.873	199 0.849	198 0.914 0.899	200 0.864	198 0.824 0.828	200 0.828	197 1.194
199 0.877	196 0.851	196 0.901	197 0.879	203 0.847 0.830	197 0.829	200 1.210
198 0.883 0.882	198 0.854 0.853	203 0.930 0.903	199 0.883	199 0.847	205 0.866 0.842	196 1.229
203 0.898 0.885	203 0.870 0.855	199 0.907	196 0.894	196 0.849	199 0.848	199 1.230
195 0.895	195 0.869	195 0.927	194 0.899	195 0.859	196 0.860	205 1.245 1.254
194 0.903	194 0.877	194 0.935	195 0.900	205 0.871 0.865	195 0.863	194 1.261
205 0.913 0.922	205 0.886 0.891	205 0.945 0.944	205 0.909 0.904	194 0.886	194 0.899	195 1.284
208 1.048 1.029	208 0.986 0.988	208 1.092 1.073	208 1.044 1.004	208 0.952 0.955	208 0.966 0.939	208 1.677 1.661
207 1.051 1.042	207 0.993 1.001	207 1.094 1.089	207 1.037 1.024	207 0.954 0.965	207 0.971 0.972	207 1.683 1.741
206 1.079 1.074	206 1.018 1.027	206 1.125 1.111	206 1.080 1.048	206 0.997 0.997	206 0.999 1.010	206 1.734 2.091
209 1.263 1.219	209 1.139 1.171	209 1.325 1.290	209 1.281 1.282	209 1.195 1.196	209 1.229 1.281	209 2.468 2.540
RT						
(min) DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil19
47 21.46	25.81	21.59	27.92	31.29	35.18	32.23
183 49.82	56.72	51.00	62.63	64.67	69.69	70.25

GC-RRTs for all peaks were calculated against the sum of the retention times (RTs) of BDEs 47 and 183. REF: reference value; PRE: predicted value. PRESS (DB-1) = 0.00053; PRESS (DB-5) = 0.00049; PRESS (HT-5) = 0.00092; PRESS (DB-17) = 0.00074; PRESS (DB-XLB) = 0.00040; PRESS (HT-8) = 0.00042; PRESS (CP-Sil 19) = 0.0045. PRESS: Predicted error sum of squares.

^aItalic is the test set included 26 BDE congeners,

^bThe bold is predicted test for 83 BDE congeners which experimental RRTs were not currently available. For predicted test of 83 BDE congeners, BDE congeners were considered to co-elute if the difference between their predicted RRTs and experimental RRTs for training and test sets was < 0.001 for peaks eluting before BDE47, and ≤ 0.002 for peaks eluting after BDE 47.

stitutional, topological, geometrical, electrostatic, and semi-empirical quantum.

GC-RRTs of 17 BDEs (4, 20, 27, 58, 72, 76, 81, 98, 103, 115, 121, 127, 158, 160, 182, 185, and 203) are included in both our test sets and predicted sets by models in ref. [21] on DB-5 stationary phase. Fig. 3 compares experimental and predicted GC-RRT of our work and Rayne's work. The curving line is experimental data (ref. [21]) versus predicted GC-RRT of Rayne's work (ref. [20]) and the linear line is experimental data (ref. [21]) versus predicted GC-RRT of this work. The fitting results show the high agreement between the different temperature programmes.

4.3. Comparison in retention behavior between PBDEs and PCBs

Based on the retention database for PCBs built by Chu and Hong [29] and retention database for PBDEs expanded

in our study (ref. [21] RRTs + Predicted RRTs), the relation of retention behavior on DB-5, DB-17 and DB-XLB column between these two classes of pollutants were studied. The best correlation coefficient for DB-5 was 0.965, for DB-17 was 0.957, and for DB-XLB was 0.960 (Fig. 4). But in fact, there were some differences that reflect the retention behavior between PCBs and PBDEs. Calculational results show that the molecules of PBDEs are not coplanar at the conformation of their lowest energy [30]. There were also some other differences; for example, our models included the descriptor "minimum electrophilic reaction index for a O atom", which indicated that O atom of PBDEs would be an important factor that reflect the elution order comparing to PCBs.

The retention time of PBDEs generally increases with the bromine substitution, with little crossover among homologs when a nonpolar stationary phase is used. In other words, PBDE congeners with $n + 1$ bromines usually elute after those with n bromines, with only a few exceptions. This is in contrast to PCBs

whose retention time order is more chaotic in regard to the degree of chlorination. This may be related to the effect of molecular planarity, which is possible for some PCB congeners but not others in the same homolog, on the chromatographic retention. Due to the steric and probably also electronic effect of the ether linkage, it is impossible for PBDEs to be planar, regardless of the number and the positions of bromines. Although the angle between the two phenyl rings at optimal conformation does differ among structural isomers depending on bromine positions [31], the effect of these difference on GC retention may be much less than the number of bromines in the molecule.

4.4. Model application

By using the models built, the RRTs of remaining 83 BDE congeners for which experimental RRTs were not currently

available were predicted, and the results were summarized in Table 3. The congeners enclosed in a box were considered co-eluting (RRTs differ by less than 0.001 before BDE47, less than 0.002 after BDE47) on specified columns.

The predicted RRTs in this work were plotted in Fig. 5 against model predicted RRTs in the ref. [20]. The plot shows a good general agreement of these two models. For the whole data matrix, the fitting curve followed the natural logarithm function due, again, to the different oven temperature programming and other operational parameters. However, for the congeners that have the same number of bromine atom, the fitting relationship is linear.

Relative retention varies with the changes in instrument configurations, column specifications, and operation conditions. In applying the established RRT models to identify the unknowns, optimal predictability is obtained only when the instrument con-

Fig. 2. Reference vs. predicted RRTs of 26 PBDE congeners in the test sets on different columns and distribution of residuals.

Fig. 2. (Continued).

Fig. 3. Comparison the RRTs of 17 PBDE congeners in the test set on DB-5 predicted by the models presented in ref. [22] and this work.

Fig. 5. Comparison between the RRTs of the 83 PBDE congeners, for which ref. RRTs are unavailable, on DB-5 predicted by the models presented in ref. [22] and this work.

(a)

(b)

(c)

Fig. 4. Retention indices based on the retention database for PCBs (ref. [32]) vs. retention database for PBDEs (database of ref. RRTs + database of predicted RRTs by our models) on DB-5, DB-17, and DB-XLB column. (a) DB-5; (b) DB-17; and (c) DB-XLB.

figuration and operation conditions are exactly the same as those used in the model development. For this reason, models for chromatographic retention prediction were often built using either isothermal or linear temperature programs [32]. However, it is practically impossible to obtain RRTs for PBDEs with isothermal or linear temperature programs, as explained in details by Rayne and Ikononou [20].

In this work, the predictability of our models was assessed using analytical results obtained under different instrument configuration and/or operation conditions. The reference RRTs used in this work were obtained by Korytár et al. [21] with the use of multi-linear temperature programs (starting at 90 °C for 2 min; 30 °C/min to 200 °C; 1.5 °C/min to 325 °C). We used two DB-5MS columns with the same diameter and film thickness as those used by Korytár et al. [21] to obtain the RRTs of selected PBDE congeners. Two runs were made with 12 and 30 m columns, respectively, on different instruments with very different temperature programs, as specified in Section 2. In addition, a set of retention times ($N = 13$) obtained by Agilent on a DB-XLB column (30 m $\times$ 0.25 mm i.d. $\times$ 0.1 μ m film thickness, constant flow at 1.2 mL min⁻¹) coupled with an ICP-MS [33] was also transformed into RRTs, which was then used as an externally obtained dataset to examine the model performance. Although the three curves in Fig. 6 are different in shape, all of them are smooth with $R > 0.995$, showing strong correlations between the two datasets. Reversal of the elution order, which was observed for several pairs of PCB congeners when oven temperature was increased at different rates [29], was not observed in this work with the limited numbers of PBDEs involved.

These observations point to the possibility of potentially high accurate predictions of RRTs using the established models. While the curvatures in Fig. 6 are most likely attributed to the differences in instrument configuration and operational parameters, the smoothness of the curves may imply that the selected PBDE congeners respond to the changes in GC parameters primarily in a systematic manner with a common mechanism. Regression equations shown in Fig. 6 can be used to “translate” the experimental RRTs into the RRTs to be used in the model, from which the unknown congeners can be identified as long as their molecular descriptors are available. Until

Fig. 6. Correlations of GC-RRTs on a DB-5 column in ref. [23] and in this work using (a) HRGC-LRMS, (b) HRGC/HRMS, and (c) Db-XLB column using GC-ICP-MS.

an approach, which is independent of instrument configuration and operation conditions, can be established, predictions of RRTs must take into consideration the impact of these variables. Simply matching the RRTs obtained with those in the reference dataset may result in faulty identification of the peaks.

5. Conclusions

Based on an experimental retention-time database of 126 PBDE congeners for seven GC columns [21], quantitative structural–retention relationship models were built to study the retention behavior on these GC columns by the heuristic method of CODESSA. The results show that the models have strong predictive abilities. The intermolecular interactions between PBDEs and the stationary phase are related to the degree of

branching of the molecules, which can be represented by Wiener or Randic index. Further, using these models, RRTs of the remaining 83 PBDEs for which retention times are currently not available, were predicted. Although nonlinear, strong correlations were obtained between RRTs obtained using different GC configurations and under different operation conditions. Once established, the correlation equations can be used to predict the chemical identities of unknown peaks.

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