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ORIGINAL PAPER

Semi-empirical topological method for prediction of the gas chromatographic relative retention times of Polybrominated Diphenyl Ethers (PBDEs)

Hong-Yan Liu · Shu-Shen Liu · Li-Tang Qin

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Abstract Quantitative structure-retention relationship (QSRR) studies have proved to be a valuable approach in the prediction of the gas chromatographic relative retention time (GC-RRT) of organic chemicals. Polybrominated diphenyl ether (PBDE) congeners are now ubiquitous environmental pollutants. Of the 209 possible PBDE congeners, 126 have been synthesized and their retention-time data on seven different stationary phases has been determined [Korytár et al.:J Chromatography A 1065:239–249, (2005)]. To estimate and predict the GC-RRT values of all 209 PBDEs on different stationary phases, 17 molecular descriptors from the semi-experience algorithm in MOPAC program and the topological structures of PBDE molecules were calculated. By means of the VSMP (variable selection and modeling based on prediction) program [Liu et al.:J Chem Inf Comput Sci 43:964–969, (2003)], six optimal descriptors were selected to develop a QSRR model for the prediction of GC-RRT of PBDE. The descriptors contain some energy information (such as the energy of the lowest unoccupied molecular orbital and highest occupied molecular orbital) and topological information (the number of *ortho*-, *meta*-, and *para*- substituted bromine atoms) as well as the molecular weight ($\ln M_W$). All the models developed were cross-validated using leave-one-out (LOO). For seven GC stationary phases, the estimated correlation coefficients (r^2) are all more than 0.985 but for the column CP-Sil 19 (r^2=0.9392) and LOO-validated correlation coefficients (q^2) all more than 0.985 but for the column CP-Sil 19 (q^2=0.9345).

Keywords Polybrominated diphenyl ethers (PBDEs) · Relative retention time(*RRT*) · Variable selection and modeling based on prediction (VSMP) · QSRR

H.-Y. Liu · L.-T. Qin
Department of Material and Chemistry Engineering,
Guilin University of Technology,
541004 Guilin, People's Republic of China

S.-S. Liu (✉)
Key Laboratory of Yangtze River Water Environment,
Ministry of Education,
College of Environmental Science and Technology,
Tongji University,
200092 Shanghai, People's Republic of China
e-mail: ssliuhl@263.net

Introduction

Polybrominated diphenyl ethers (PBDEs), which constitute one group of chemical substances used as additive flame retardants, have the chemical formula $C_{12}H_{(10-n)}Br_{(n)}O$ ($1 \leq n \leq 10$), the theoretical number of possible congeners 209, and the characteristics very similar to those of the polychlorinated biphenyls (PCBs) [1] as shown in Fig. 1. Moreover, the IUPAC numbering scheme for polychlorinated biphenyl (PCB) congeners is also used for PBDEs [2]. PBDEs have been used extensively over the past two decades as flame or fire retardants that are added to manufactured products such as textiles, electronic equipment and insulation materials [3, 4]. PBDEs are now ubiquitous environmental pollutants and have been detected in biotic and abiotic matrices including fish, birds, sediments, air, marine mammals and human plasma and milk et al. [5–8]. They are associated with adverse health effects such as immune suppression, altering sexual differentiation, mutagenicity and carcinogenicity [9, 10]. It is necessary to identify and monitor the concentrations of all PBDE congeners in environmental matrices. The lack of standards is a major impediment to chemical analysis and property determination. There were few physical-chemical properties

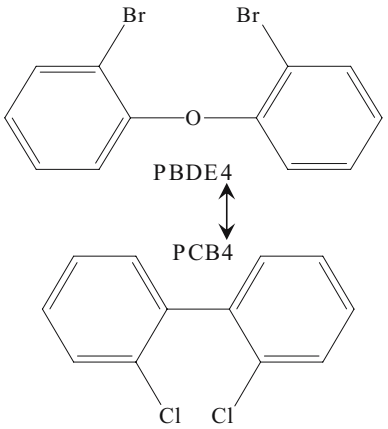

Fig. 1 Similarity between the structure of PBDE and PCB molecule

that have been measured. So it is important to develop predictive models for physicochemical properties of PBDEs from their molecular structures.

The gas chromatographic retention index (GC-RI) can be used for distinguishing the isomer of compounds. The GC relative retention time (*RRT*) is an unique characteristic of the solute and can be used for identification purposes. However, there are a lack of GC-*RRT* values for most of the PBDE congeners. At present, of the 209 possible PBDE congeners, 126 have been synthesized [11] and their retention-time data on seven different stationary phases has been determined. There are also several reports on the prediction of RRT for PBDEs. Rayne et al. [12] proposed an estimation model derived from the gas chromatographic relative retention times (GC-*RRT*) of 46 PBDE congeners on the DB-5 column of GC. In the model, however, the number of hepta- and octa-PBDE congeners are too small (3 and 0, respectively) and only one GC stationary phases (DB-5). Liu et al. used the molecular electronegativity distance vector (MEDV) [13–15] directly from the molecular structure to correlate with the GC-*RRTs* of 46 PBDE congeners [16]. Wang et al. [17, 18] reported the toxicity models as well as *GC-RRT* ones relating with the molecular descriptors of PBDEs congeners.

In this paper, we propose a semi-empirical topological method for the prediction of the *RRTs* of PBDEs. Selecting some semi-empirical quantum chemical descriptors such as the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and the energy of the highest occupied molecular orbital (E_{HOMO}) as well as the number of substitueted bromine atoms as descriptors, the quantitative structure-retention relationship (QSRR) models correlating to the *RRT*s of 126 PBDE congeners are developed using the VSMP (variable selection and modeling based on prediction) [19–21]. It has been found that the QSRR models have not only high estimation qualities and high stabilities but also good predictive potentials.

Data set

The observed GC-*RRTs* of 126 PBDEs on seven different stationary phases were directly taken from the literature [11] and the GC-*RRT*s designed as a dependent variable. The empirical formula, names, the CAS RN (Chemical Abstracts Services Registry Number) and the GC-RRT values of the compounds were listed in Table 1.

The structures of all 209 PBDE congeners are characterized using 17 molecular descriptors (see Table 2). Here, 8 quantum chemical descriptors, i.e., the dipole moment of the molecules (μ), the heat of formation (H_f), the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), E^2_{HOMO}, E^2_{LUMO}, the largest negative net atomic charge in molecule (q^-), and the most positive net atomic charges on a hydrogen atom ($q\mathrm{H}^?$), were computed by the MOPAC-AM1 module included in the CS Chem3D Ultra 9.0 soft package; 4 theoretical descriptors, total energy (*TE*), molecular weight (M_w), the natural logarithm of molecular weight ($\ln M_w$), and common logarithm of the octanol-water partition coefficient ($\log P$), were calculated by the ChemPropPro module in the above package; and the other 5 descriptors, the number of ortho-substituted bromines (*o*-Br), meta-substituted bromines (*m*-Br) and para-substituted bromines (*p*-Br), the square root of the number of bromine substituents ($\mathrm{Br}^{1/2}$) and the number of bromine substituents (Br^{2}), belonged to topological-type ones.

Some of the above descriptors expressed the electronic structure-related information. For example, E_{HOMO} and q^- imply the electron-donating ability, E_{LUMO} and $q\mathrm{H}^+$ denote electron-acceptance ability, μ refers to molecular dipolar property, H_f is the heat released or absorbed (enthalpy change) during the formation of a pure substance from its elements at constant pressure. The other ones reflected the molecular size and topological information such as Mw, *o*-Br, *m*-Br, and *p*-Br. Furthermore, logarithm transferation and square operation is to add some nonlinear components in linear model. The descriptors were designed as independent variables (predictors).

To validate the predictive power of QSRR model, 84 PBDEs are selected from a pool of 126 PBDEs to construct a training set, and the remaining 42 PBDEs form a test set. The best model developed by the training set is used to predict the *GC-RRT* values of the PBDEs in the test set.

QSRR model of 126 PBDEs on DB-1 column

Selecting 17 descriptors including 8 quantum chemical parameters, 4 theoretical descriptors, and 5 other ones as independent variables and the GC-*RRT* values of 126 PBDE on DB-1 column as a dependent one, the best combination of variables is optimized by the VSMP

Table 1 The empirical formula, names, the CAS number , and the GC-RRT values of PBDEs

No.	PBDE	CASRN	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
1	2-Br	36563-47-0	0.100	0.095	0.091	0.087	0.086	0.084	0.083
2	3-Br	6876-00-2	0.102	0.097	0.091	0.086	0.088	0.085	0.083
3	4-Br	101-55-3	0.103	0.099	0.093	0.088	0.090	0.087	0.086
4	2,2′-diBr	51452-87-0	0.134	0.133	0.122	0.129	0.127	0.131	0.130
5	2,3-diBr								
6	2,3′-diBr	147217-72-9	0.135	0.134	0.121	0.125	0.128	0.130	0.127
7	2,4-diBr	171977-44-9	0.134	0.133	0.121	0.122	0.128	0.129	0.125
8	2,4′-diBr	147217-71-8	0.139	0.139	0.126	0.129	0.135	0.137	0.134
9	2,5-diBr		0.131	0.129	0.116	0.117	0.123	0.122	0.120
10	2,6-diBr	51930-04-2	0.125	0.123	0.112	0.117	0.117	0.116	0.116
11	3,3′-diBr	6903-63-5	0.139	0.137	0.124	0.124	0.133	0.134	0.130
12	3,4-diBr	189084-59-1	0.142	0.142	0.128	0.129	0.138	0.139	0.135
13	3,4′-diBr	83694-71-7	0.142	0.142	0.128	0.129	0.140	0.140	0.136
14	3,5-diBr		0.133	0.130	0.117	0.114	0.124	0.124	0.118
15	4,4′-diBr	62962-84-9	0.146	0.147	0.133	0.133	0.147	0.147	0.142
16	2,2′,3-triBr		0.207	0.214	0.193	0.209	0.218	0.226	0.217
17	2,2′,4-triBr	147217-75-2	0.196	0.202	0.183	0.199	0.205	0.214	0.206
18	2,2′,5-triBr		0.186	0.191	0.169	0.188	0.192	0.196	0.193
19	2,2′,6-triBr		0.181	0.187	0.168	0.194	0.186	0.196	0.193
20	2,3,3′-triBr		0.214	0.221	0.201	0.209	0.228	0.235	0.223
21	2,3,4-triBr								
22	2,3,4′-triBr		0.223	0.231	0.211	0.221	0.242	0.247	0.235
23	2,3,5-triBr								
24	2,3,6-triBr								
25	2,3′,4-triBr	147217-77-4	0.198	0.204	0.182	0.195	0.208	0.213	0.204
26	2,3′,5-triBr		0.190	0.195	0.172	0.184	0.198	0.200	0.194
27	2,3′,6-triBr		0.180	0.184	0.162	0.184	0.184	0.188	0.185
28	2,4,4′-triBr	41318-75-6	0.207	0.214	0.194	0.206	0.223	0.227	0.216
29	2,4,5-triBr		0.193	0.197	0.173	0.186	0.198	0.202	0.193
30	2,4,6-triBr	155999-95-4	0.172	0.174	0.152	0.166	0.174	0.175	0.167
31	2,4′,5-triBr		0.199	0.205	0.182	0.195	0.212	0.213	0.206
32	2,4′,6-triBr	189084-60-4	0.190	0.195	0.175	0.191	0.199	0.205	0.197
33	2,3′,4′-triBr	147217-78-5	0.207	0.214	0.193	0.210	0.218	0.226	0.218
34	2,3′,5′-triBr		0.188	0.192	0.169	0.179	0.196	0.196	0.189
35	3,3′,4-triBr	147217-80-9	0.215	0.221	0.201	0.209	0.228	0.235	0.224
36	3,3′,5-triBr		0.196	0.199	0.178	0.177	0.203	0.206	0.194
37	3,4,4′-triBr	147217-81-0	0.223	0.232	0.211	0.221	0.242	0.247	0.236
38	3,4,5-triBr		0.212	0.217	0.193	0.204	0.220	0.226	0.214
39	3,4′,5-triBr		0.203	0.208	0.186	0.189	0.215	0.217	0.205
40	2,2′,3,3′-tetraBr		0.344	0.355	0.347	0.351	0.372	0.380	0.360
41	2,2′,3,4-tetraBr								
42	2,2′,3,4′-tetraBr		0.317	0.329	0.313	0.327	0.343	0.350	0.332
43	2,2′,3,5-tetraBr								
44	2,2′,3,5′-tetraBr								
45	2,2′,3,6-tetraBr								
46	2,2′,3,6′-tetraBr		0.287	0.299	0.275	0.306	0.306	0.315	0.304
47	2,2′,4,4′-tetraBr	5436-43-1	0.301	0.313	0.297	0.308	0.326	0.335	0.315
48	2,2′,4,5-tetraBr		0.287	0.298	0.272	0.298	0.304	0.313	0.298
49	2,2′,4,5′-tetraBr	243982-82-3	0.283	0.294	0.269	0.290	0.305	0.309	0.296
50	2,2′,4,6-tetraBr		0.261	0.272	0.247	0.278	0.278	0.287	0.272
51	2,2′,4,6′-tetraBr		0.278	0.289	0.271	0.296	0.296	0.311	0.296
52	2,2′,5,5′-tetraBr								
53	2,2′,5,6′-tetraBr		0.253	0.264	0.232	0.275	0.268	0.272	0.269
54	2,2′,6,6′-tetraBr								
55	2,3,3′,4-tetraBr		0.328	0.341	0.326	0.349	0.356	0.363	0.347
56	2,3,3′,4′-tetraBr								

Table 1 (continued)

No.	PBDE	CASRN	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
57	2,3,3′,5-tetraBr								
58	2,3,3′,5′-tetraBr		0.312	0.321	0.304	0.302	0.335	0.341	0.319
59	2,3,3′,6-tetraBr								
60	2,3,4,4′-tetraBr	40088-47-9							
61	2,3,4,5-tetraBr								
62	2,3,4,6-tetraBr		0.277	0.287	0.256	0.291	0.296	0.297	0.283
63	2,3,4′,5-tetraBr								
64	2,3,4′,6-tetraBr								
65	2,3,5,6-tetraBr								
66	2,3′,4,4′-tetraBr	189084-61-5	0.316	0.328	0.313	0.326	0.343	0.350	0.332
67	2,3′,4,5-tetraBr		0.294	0.303	0.279	0.294	0.312	0.318	0.301
68	2,3′,4,5′-tetraBr		0.285	0.294	0.270	0.280	0.305	0.308	0.290
69	2,3′,4,6-tetraBr	327185-09-1	0.258	0.268	0.238	0.265	0.274	0.278	0.264
70	2,3′,4′,5-tetraBr								
71	2,3′,4′,6-tetraBr	189084-62-6	0.287	0.299	0.275	0.306	0.306	0.315	0.303
72	2,3′,5,5′-tetraBr		0.274	0.281	0.253	0.261	0.289	0.291	0.277
73	2,3′,5′,6-tetraBr		0.257	0.266	0.234	0.262	0.269	0.273	0.264
74	2,4,4′,5-tetraBr		0.309	0.319	0.299	0.310	0.334	0.338	0.318
75	2,4,4′,6-tetraBr	189084-63-7	0.278	0.290	0.271	0.296	0.296	0.311	0.296
76	2,3′,4′,5′-tetraBr		0.311	0.322	0.300	0.322	0.329	0.339	0.322
77	3,3′,4,4′-tetraBr	93703-48-1	0.343	0.355	0.347	0.350	0.372	0.380	0.359
78	3,3′,4,5-tetraBr		0.325	0.334	0.318	0.322	0.346	0.354	0.333
79	3,3′,4,5′-tetraBr		0.312	0.321	0.304	0.302	0.335	0.341	0.320
80	3,3′,5,5′-tetraBr		0.284	0.289	0.267	0.255	0.299	0.304	0.281
81	3,4,4′,5-tetraBr		0.339	0.350	0.335	0.344	0.365	0.370	0.349
82	2,2′,3,3′,4-pentaBr								
83	2,2′,3,3′,5-pentaBr								
84	2,2′,3,3′,6-pentaBr								
85	2,2′,3,4,4′-pentaBr	182346-21-0	0.476	0.486	0.498	0.500	0.499	0.508	0.479
86	2,2′,3,4,5-pentaBr		0.452	0.462	0.455	0.478	0.466	0.475	0.453
87	2,2′,3,4,5′-pentaBr		0.450	0.460	0.457	0.471	0.473	0.476	0.456
88	2,2′,3,4,6-pentaBr		0.411	0.423	0.409	0.444	0.431	0.438	0.416
89	2,2′,3,4,6′-pentaBr								
90	2,2′,3,4′,5-pentaBr								
91	2,2′,3,4′,6-pentaBr								
92	2,2′,3,5,5′-pentaBr								
93	2,2′,3,5,6-pentaBr								
94	2,2′,3,5,6′-pentaBr								
95	2,2′,3,5′,6-pentaBr								
96	2,2′,3,6,6′-pentaBr								
97	2,2′,3,4′,5′-pentaBr		0.450	0.457	0.455	0.452	0.469	0.472	0.446
98	2,2′,3,4′,6′-pentaBr		0.405	0.414	0.400	0.414	0.423	0.428	0.403
99	2,2′,4,4′,5-pentaBr	60348-60-9	0.425	0.433	0.424	0.430	0.443	0.447	0.422
100	2,2′,4,4′,6-pentaBr	189084-64-8	0.395	0.405	0.396	0.403	0.413	0.424	0.394
101	2,2′,4,5,5′-pentaBr		0.401	0.410	0.389	0.403	0.418	0.418	0.400
102	2,2′,4,5,6′-pentaBr		0.385	0.396	0.370	0.408	0.396	0.404	0.389
103	2,2′,4,5′,6-pentaBr		0.358	0.369	0.336	0.372	0.374	0.373	0.360
104	2,2′,4,6,6′-pentaBr		0.357	0.369	0.344	0.383	0.373	0.382	0.359
105	2,3,3′,4,4′-pentaBr		0.496	0.506	0.519	0.519	0.519	0.524	0.500
106	2,3,3′,4,5-pentaBr		0.461	0.469	0.464	0.472	0.477	0.481	0.457
107	2,3,3′,4′,5-pentaBr								
108	2,3,3′,4,5′-pentaBr		0.451	0.461	0.456	0.460	0.473	0.474	0.450
109	2,3,3′,4,6-pentaBr		0.406	0.417	0.395	0.427	0.427	0.425	0.407
110	2,3,3′,4′,6-pentaBr								
111	2,3,3′,5,5′-pentaBr								
112	2,3,3′,5,6-pentaBr								

Table 1 (continued)

No.	PBDE	CASRN	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
113	2,3,3′,5′,6-pentaBr								
114	2,3,4,4′,5-pentaBr		0.483	0.491	0.494	0.495	0.503	0.505	0.478
115	2,3,4,4′,6-pentaBr		0.434	0.442	0.435	0.445	0.457	0.458	0.430
116	2,3,4,5,6-pentaBr	189084-65-9	0.434	0.444	0.424	0.463	0.454	0.452	0.430
117	2,3,4′,5,6-pentaBr								
118	2,3′,4,4′,5-pentaBr		0.450	0.457	0.455	0.452	0.469	0.472	0.447
119	2,3′,4,4′,6-pentaBr	189084-66-0	0.405	0.414	0.400	0.416	0.423	0.428	0.403
120	2,3′,4,5,5′-pentaBr	417727-71-0	0.408	0.414	0.398	0.394	0.423	0.424	0.400
121	2,3′,4,5′,6-pentaBr		0.363	0.371	0.339	0.362	0.377	0.375	0.356
122	2,3,3′,4′,5′-pentaBr								
123	2,3′,4,4′,5′-pentaBr		0.453	0.462	0.459	0.462	0.471	0.476	0.449
124	2,3′,4′,5,5′-pentaBr		0.436	0.443	0.432	0.435	0.453	0.454	0.432
125	2,3′,4′,5′,6-pentaBr		0.414	0.424	0.403	0.436	0.426	0.431	0.415
126	3,3′,4,4′,5-pentaBr		0.490	0.495	0.507	0.489	0.508	0.513	0.485
127	3,3′,4,5,5′-pentaBr		0.449	0.454	0.453	0.430	0.465	0.469	0.439
128	2,2′,3,3′,4,4′-hexaBr		0.679	0.677	0.730	0.702	0.680	0.682	0.704
129	2,2′,3,3′,4,5-hexaBr								
130	2,2′,3,3′,4,5′-hexaBr								
131	2,2′,3,3′,4,6-hexaBr		0.586	0.586	0.598	0.595	0.590	0.586	0.562
132	2,2′,3,3′,4,6′-hexaBr								
133	2,2′,3,3′,5,5′-hexaBr								
134	2,2′,3,3′,5,6-hexaBr								
135	2,2′,3,3′,5,6′-hexaBr								
136	2,2′,3,3′,6,6′-hexaBr								
137	2,2′,3,4,4′,5-hexaBr	446254-95-1							
138	2,2′,3,4,4′,5′-hexaBr	182677-30-1	0.618	0.617	0.644	0.626	0.619	0.620	0.605
139	2,2′,3,4,4′,6-hexaBr		0.576	0.577	0.595	0.610	0.579	0.584	0.551
140	2,2′,3,4,4′,6′-hexaBr	243982-83-4	0.586	0.588	0.614	0.603	0.588	0.597	0.565
141	2,2′,3,4,5,5′-hexaBr		0.587	0.585	0.594	0.588	0.586	0.582	0.563
142	2,2′,3,4,5,6-hexaBr		0.595	0.598	0.610	0.624	0.597	0.599	0.578
143	2,2′,3,4,5,6′-hexaBr								
144	2,2′,3,4,5′,6-hexaBr		0.528	0.531	0.516	0.543	0.533	0.524	0.507
145	2,2′,3,4,6,6′-hexaBr								
146	2,2′,3,4′,5,5′-hexaBr								
147	2,2′,3,4′,5,6-hexaBr								
148	2,2′,3,4′,5,6′-hexaBr								
149	2,2′,3,4′,5′,6-hexaBr								
150	2,2′,3,4′,6,6′-hexaBr								
151	2,2′,3,5,5′,6-hexaBr								
152	2,2′,3,5,6,6′-hexaBr								
153	2,2′,4,4′,5,5′-hexaBr	68631-49-2	0.563	0.560	0.564	0.552	0.560	0.558	0.531
154	2,2′,4,4′,5,6′-hexaBr	207122-15-4	0.515	0.517	0.504	0.518	0.513	0.513	0.487
155	2,2′,4,4′,6,6′-hexaBr	35854-94-5	0.491	0.496	0.483	0.500	0.494	0.497	0.462
156	2,3,3′,4,4′,5-hexaBr		0.644	0.640	0.672	0.643	0.642	0.640	0.637
157	2,3,3′,4,4′,5′-hexaBr								
158	2,3,3′,4,4′,6-hexaBr		0.586	0.587	0.598	0.597	0.590	0.586	0.563
159	2,3,3′,4,5,5′-hexaBr		0.593	0.590	0.603	0.578	0.591	0.587	0.564
160	2,3,3′,4,5,6-hexaBr		0.589	0.590	0.592	0.609	0.592	0.584	0.567
161	2,3,3′,4,5′,6-hexaBr		0.533	0.535	0.521	0.534	0.536	0.526	0.505
162	2,3,3′,4′,5,5′-hexaBr								
163	2,3,3′,4′,5,6-hexaBr								
164	2,3,3′,4′,5′,6-hexaBr								
165	2,3,3′,5,5′,6-hexaBr								
166	2,3,4,4′,5,6-hexaBr	189084-58-0	0.623	0.621	0.643	0.631	0.627	0.622	0.603
167	2,3′,4,4′,5,5′-hexaBr		0.600	0.596	0.613	0.588	0.596	0.594	0.572
168	2,3′,4,4′,5′,6-hexaBr		0.547	0.548	0.543	0.551	0.545	0.543	0.515

Table 1 (continued)

No.	PBDE	CASRN	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
169	3,3′,4,4′,5,5′-hexaBr								
170	2,2′,3,3′,4,4′,5-heptaBr	327185-13-7							
171	2,2′,3,3′,4,4′,6-heptaBr								
172	2,2′,3,3′,4,5,5′-heptaBr								
173	2,2′,3,3′,4,5,6-heptaBr		0.779	0.763	0.807	0.776	0.755	0.743	0.850
174	2,2′,3,3′,4,5,6′-heptaBr								
175	2,2′,3,3′,4,5′,6-heptaBr								
176	2,2′,3,3′,4,6,6′-heptaBr								
177	2,2′,3,3′,4,5′,6′-heptaBr								
178	2,2′,3,3′,5,5′,6-heptaBr								
179	2,2′,3,3′,5,6,6′-heptaBr								
180	2,2′,3,4,4′,5,5′-heptaBr								
181	2,2′,3,4,4′,5,6-heptaBr		0.770	0.754	0.807	0.761	0.744	0.742	0.823
182	2,2′,3,4,4′,5,6′-heptaBr		0.707	0.697	0.717	0.708	0.68	0.675	0.696
183	2,2′,3,4,4′,5′,6-heptaBr	207122-16-5	0.699	0.687	0.703	0.692	0.674	0.665	0.685
184	2,2′,3,4,4′,6,6′-heptaBr		0.673	0.666	0.683	0.679	0.654	0.652	0.636
185	2,2′,3,4,5,5′,6-heptaBr		0.713	0.702	0.716	0.714	0.693	0.676	0.722
186	2,2′,3,4,5,6,6′-heptaBr								
187	2,2′,3,4′,5,5′,6-heptaBr								
188	2,2′,3,4′,5,6,6′-heptaBr								
189	2,3,3′,4,4′,5,5′-heptaBr								
190	2,3,3′,4,4′,5,6-heptaBr		0.780	0.763	0.807	0.778	0.755	0.742	0.852
191	2,3,3′,4,4′,5′,6-heptaBr		0.734	0.721	0.744	0.729	0.708	0.695	0.746
192	2,3,3′,4,5,5′,6-heptaBr		0.721	0.707	0.720	0.710	0.698	0.678	0.722
193	2,3,3′,4′,5,5′,6-heptaBr								
194	2,2′,3,3′,4,4′,5,5′-octaBr	85446-17-9							
195	2,2′,3,3′,4,4′,5,6-octaBr								
196	2,2′,3,3′,4,4′,5,6′-octaBr								
197	2,2′,3,3′,4,4′,6,6′-octaBr								
198	2,2′,3,3′,4,5,5′,6-octaBr		0.882	0.853	0.899	0.860	0.828	0.809	1.094
199	2,2′,3,3′,4,5,5′,6′-octaBr								
200	2,2′,3,3′,4,5,6,6′-octaBr								
201	2,2′,3,3′,4,5′,6,6′-octaBr								
202	2,2′,3,3′,5,5′,6,6′-octaBr								
203	2,2′,3,4,4′,5,5′,6-octaBr		0.885	0.855	0.903	0.859	0.830	0.812	1.100
204	2,2′,3,4,4′,5,6,6′-octaBr	446255-54-5	0.858	0.834	0.885	0.849	0.810	0.801	0.981
205	2,3,3′,4,4′,5,5′,6-octaBr		0.922	0.891	0.944	0.904	0.865	0.842	1.254
206	2,2′,3,3′,4,4′,5,5′,6-nonaBr		1.074	1.027	1.111	1.048	0.997	1.009	2.091
207	2,2′,3,3′,4,4′,5,6,6′-nonaBr		1.042	1.001	1.089	1.024	0.965	0.972	1.741
208	2,2′,3,3′,4,5,5′,6,6′-nonaBr	876310-29-1	1.029	0.988	1.073	1.004	0.955	0.939	1.661
209	Decabromobiphenyl ether	1163-19–5	1.219	1.171	1.290	1.282	1.196	1.281	2.540

Table 2 17 molecular descriptors and denotations

Descriptor	Variable	Descriptor	Variable
Log$P$	x_1	q^-	x_{10}
Mw	x_2	E^2_{HOMO}	x_{11}
$\ln M_W$	x_3	E^2_{LUMO}	x_{12}
H_f	x_4	o-Br	x_{13}
TE	x_5	m-Br	x_{14}
E_{HOMO}	x_6	p-Br	x_{15}
E_{LUMO}	x_7	Br^2	x_{16}
μ	x_8	$Br^{1/2}$	x_{17}
qH^+	x_9		

program [19–21]. The qualities of the models derived from various subsets are evaluated using some statistics, such as the calibrated correlation coefficient (r) and root mean square error (*RMSE*) in the model development, the validated correlation coefficient (q) and root mean square error (*RMSV*) in the leave-one-out (LOO) cross-validation. Some statistic results of optimal models developed using different variable subsets are listed in Table 3. From Table 3, the value of q^2 is the highest and *RMSV* the lowest when the number of optimal variables (m) in QSRR equals to 6, which implies an optimal subset consisting of 6

Table 3 Some statistic results for QSRR models of PBDEs on DB-1 column

m	r^2	*r*	*RMSV*	q^2	*q*	*RMSE*	Variables
1	0.9739	0.9868	0.038	0.9711	0.9854	0.040	$\boldsymbol{x}_{16}$
2	0.9777	0.9888	0.035	0.9748	0.9873	0.037	$\boldsymbol{x}_{15}$, $\boldsymbol{x}_{16}$
3	0.9844	0.9922	0.029	0.9819	0.9909	0.031	$\boldsymbol{x}_{14}$, $\boldsymbol{x}_{15}$, $\boldsymbol{x}_{16}$
4	0.9887	0.9944	0.025	0.9876	0.9938	0.026	$\boldsymbol{x}_{3}$, $\boldsymbol{x}_{13}$, $\boldsymbol{x}_{14}$, $\boldsymbol{x}_{15}$
5	0.9908	0.9954	0.022	0.9897	0.9948	0.024	$\boldsymbol{x}_{3}$, $\boldsymbol{x}_{11}$, $\boldsymbol{x}_{13}$, $\boldsymbol{x}_{14}$, $\boldsymbol{x}_{15}$
6	0.9920	0.9960	0.021	0.9907	0.9953	0.022	$\boldsymbol{x}_{3}$, $\boldsymbol{x}_{11}$, $\boldsymbol{x}_{12}$, $\boldsymbol{x}_{13}$, $\boldsymbol{x}_{14}$, $\boldsymbol{x}_{15}$
7	0.9921	0.9961	0.021	0.9907	0.9954	0.022	$\boldsymbol{x}_{3}$, $\boldsymbol{x}_{9}$, $\boldsymbol{x}_{11}$, $\boldsymbol{x}_{12}$, $\boldsymbol{x}_{13}$, $\boldsymbol{x}_{14}$, $\boldsymbol{x}_{15}$

variables of nos. 3, 11, 12, 13, 14, and 15. The optimal variables are corresponding with $\ln M_W$, E^2_{HOMO}, E^2_{LUMO}, *o*-Br, *m*-Br, and *p*-Br, respectively. The 6-variable QSRR model (noted as M1) is written as follows.

$$\begin{aligned}\mathrm{RRT} = {} & (5.7733 \pm 0.2980) - (1.0493 \pm 0.0521)\ \cdot x_3 \\ & -(0.002192 \pm 0.000314)\ \cdot x_{11} \\ & -(0.04835 \pm 0.01111)\ \cdot x_{12} \\ & +(0.2726 \pm 0.0104)\ \cdot x_{13} \\ & +(0.3148 \pm 0.0117)\ \cdot x_{14} \\ & +(0.3220 \pm 0.0120)\ \cdot x_{15}\end{aligned} \tag{1}$$

$$\begin{aligned}& n = 126,\ m = 6,\ r^2 = 0.9920,\ r = 0.9960, \\ & RMSE = 0.021,\ F = 2466.0\ \text{(Estimation)} \\ & n = 126,\ m = 6,\ q^2 = 0.9907,\ q = 0.9953, \\ & RMSV = 0.022\quad \text{(LOO validation)}\end{aligned}$$

Where *n* is the number of samples used to build a model, *m* the number of variables in an optimal model, and *F* Fisher's statistic. The value after the symbol "±" in the parentheses is the standard derivation related to the regression coefficient. Obviously, the M1 model has an excellent estimation ability and stability.

It was found that the PCB with one or more ortho-substituted chloride atoms has a different effect on the GC-RRT from the other PCB molecules [22]. From Table 1, it can also be found that the greater the number of ortho-substituted bromine atoms, the smaller the RRT value of the PBDE having the same formula. For example, the RRT value of 2,2′,4,4′,6,6′-BDE is the least among those PBDEs of nos.128 to169 with the same formula. Again, 2,2′,3,4,4′,6,6′-BDE among those PBDEs of nos. 170 to 193 and 2,2′,3,4,4′,5,6,6′-BDE among those PBDEs of nos. 194 to 205 have the least RRT values, respectively. The facts above showed that the descriptor (x_{13}) related to ortho-substituted effect is an important factor affecting the RRT value. The descriptor is also one of 6 optimal ones chosen by VSMP program.

A good QSRR model should has not only excellent estimation ability for the internal example but also good predictive power for the external example. In order to validate the predictive ability of the model (M1), an optimal variable selection is performed on the training set including 84 PBDEs using VSMP program the same as the global data set of 126 PBDEs. The results show that the best model is still a 6-variable model (Eq. 2) consisting of the descriptors of nos. 3, 11, 12, 13, 14, and 15. The model (noted as MT1) is then used to predict the RRTs of 42 PBDEs in the test set (samples with "*" in Table 4). From Eq. 2, the MT1 model has not only an excellent estimated ability of r=0.9967 and *RMSE*=0.019 as well as a high stability of q=0.9956 and *RMSV*=0.022 but also a good predictive potential of u=0.9946 and *RMSP*=0.025.

$$\begin{aligned}\mathrm{RRT} = {} & (5.4590 \pm 0.3525) - (0.9956 \pm 0.0615)\ \cdot x_3 \\ & -(0.001788 \pm 0.000377)\ \cdot x_{11} \\ & -(0.03002 \pm 0.01347)\ \cdot x_{12} \\ & +(0.2582 \pm 0.0124)\ \cdot x_{13} \\ & +(0.2980\ \pm 0.0141)\ \cdot x_{14} + (0.3067 \pm 0.0142)\ \cdot x_{15}\end{aligned} \tag{2}$$

$$\begin{aligned}& n = 84,\ m = 6,\ r^2 = 0.9933,\ r = 0.9967, \\ & RMSE = 0.919,\ F = 1909.5\ \text{(Estimation)} \\ & n = 84,\ m = 6,\ q^2 = 0.9912,\ q = 0.9956, \\ & RMSV = 0.022\quad \text{(LOO validation)} \\ & n = 84,\ u^2 = 0.9892,\ u = 0.9946, \\ & RMSP = 0.025\ \ \text{(Test prediction)}\end{aligned}$$

Three parameters, n_t, u, and *RMSP*, in Eq. 2 refer to the number of samples in test set, predicted correlation coefficient, and predicted root mean square error, respectively.

Table 4 GC-RRT values of PBDEs observed and calculated by the models such as M1~M7 and MT1~MT7

No	DB-1			DB-5			HT-5			DB-17			DB-XLB			HT-8			CP-Sil 19		
	OBS	M1	MT1	OBS	M2	MT2	OBS	M3	MT3	OBS	M4	MT4	OBS	M5	MT5	OBS	M6	MT6	OBS	M7	MT7
1	0.100	0.117	0.112	0.095	0.101	0.096	0.091	0.111	0.108	0.087	0.098	0.100	0.086	0.085	0.086	0.084	0.090	0.097	0.083	0.304	0.225
2*	0.102	0.111	0.111	0.097	0.093	0.093	0.091	0.100	0.103	0.086	0.082	0.087	0.088	0.078	0.082	0.085	0.081	0.092	0.083	0.314	0.253
3	0.103	0.119	0.121	0.099	0.104	0.101	0.093	0.114	0.117	0.088	0.096	0.100	0.090	0.090	0.090	0.087	0.095	0.101	0.086	0.300	0.254
4	0.134	0.124	0.116	0.133	0.127	0.123	0.122	0.111	0.106	0.129	0.128	0.124	0.127	0.126	0.125	0.131	0.131	0.133	0.130	0.131	0.141
5		0.133	0.129		0.135	0.133		0.119	0.116		0.126	0.124		0.134	0.135		0.137	0.141		0.155	0.169
6*	0.135	0.126	0.124	0.134	0.126	0.127	0.121	0.109	0.107	0.125	0.116	0.114	0.128	0.125	0.127	0.130	0.128	0.132	0.127	0.152	0.169
7	0.134	0.135	0.134	0.133	0.138	0.135	0.121	0.124	0.122	0.122	0.131	0.129	0.128	0.138	0.136	0.129	0.143	0.143	0.125	0.138	0.170
8*	0.139	0.129	0.130	0.139	0.131	0.130	0.126	0.116	0.115	0.129	0.123	0.121	0.135	0.131	0.129	0.137	0.136	0.135	0.134	0.136	0.170
9	0.131	0.128	0.126	0.129	0.129	0.129	0.116	0.113	0.110	0.117	0.120	0.118	0.123	0.128	0.130	0.122	0.131	0.135	0.120	0.153	0.169
10	0.125	0.089	0.088	0.123	0.092	0.094	0.112	0.066	0.068	0.117	0.089	0.085	0.117	0.088	0.091	0.116	0.093	0.097	0.116	0.112	0.141
11	0.139	0.130	0.129	0.137	0.130	0.132	0.124	0.111	0.115	0.124	0.114	0.115	0.133	0.130	0.135	0.134	0.131	0.139	0.130	0.165	0.197
12	0.142	0.136	0.138	0.142	0.138	0.138	0.128	0.122	0.126	0.129	0.124	0.125	0.138	0.139	0.139	0.139	0.142	0.145	0.135	0.151	0.197
13	0.142	0.137	0.139	0.142	0.139	0.139	0.128	0.124	0.128	0.129	0.126	0.126	0.140	0.140	0.141	0.140	0.144	0.147	0.136	0.151	0.197
14*	0.133	0.124	0.126	0.130	0.124	0.128	0.117	0.104	0.109	0.114	0.107	0.108	0.124	0.123	0.129	0.124	0.125	0.132	0.118	0.164	0.197
15*	0.146	0.144	0.147	0.147	0.147	0.145	0.133	0.135	0.139	0.133	0.136	0.136	0.147	0.149	0.146	0.147	0.155	0.153	0.142	0.136	0.198
16	0.207	0.193	0.186	0.214	0.203	0.201	0.193	0.178	0.174	0.209	0.200	0.196	0.218	0.208	0.209	0.226	0.211	0.213	0.217	0.142	0.155
17*	0.196	0.214	0.208	0.202	0.225	0.219	0.183	0.207	0.199	0.199	0.224	0.218	0.205	0.231	0.227	0.214	0.236	0.231	0.206	0.140	0.155
18*	0.186	0.205	0.199	0.191	0.214	0.211	0.169	0.193	0.184	0.188	0.209	0.205	0.192	0.219	0.219	0.196	0.222	0.221	0.193	0.155	0.155
19	0.181	0.170	0.164	0.187	0.181	0.180	0.168	0.152	0.147	0.194	0.185	0.177	0.186	0.184	0.184	0.196	0.189	0.189	0.193	0.115	0.127
20*	0.214	0.203	0.200	0.221	0.211	0.212	0.201	0.187	0.186	0.209	0.200	0.198	0.228	0.217	0.220	0.235	0.219	0.222	0.223	0.166	0.182
21		0.215	0.212		0.225	0.223		0.206	0.204		0.218	0.215		0.233	0.231		0.236	0.235		0.152	0.183
22	0.223	0.206	0.206	0.231	0.215	0.215	0.211	0.194	0.193	0.221	0.206	0.203	0.242	0.222	0.222	0.247	0.226	0.224	0.235	0.149	0.183
23		0.206	0.202		0.214	0.214		0.191	0.189		0.203	0.202		0.220	0.223		0.222	0.225		0.166	0.182
24		0.168	0.165		0.177	0.179		0.145	0.147		0.173	0.168		0.181	0.184		0.184	0.187		0.126	0.155
25	0.198	0.204	0.204	0.204	0.213	0.213	0.182	0.191	0.190	0.195	0.203	0.200	0.208	0.220	0.219	0.213	0.223	0.222	0.204	0.149	0.183
26	0.190	0.197	0.196	0.195	0.204	0.206	0.172	0.179	0.178	0.184	0.191	0.189	0.198	0.209	0.213	0.200	0.211	0.214	0.194	0.164	0.182
27	0.180	0.158	0.158	0.184	0.167	0.172	0.162	0.133	0.136	0.184	0.162	0.156	0.184	0.170	0.175	0.188	0.173	0.176	0.185	0.123	0.155
28*	0.207	0.207	0.210	0.214	0.217	0.216	0.194	0.197	0.197	0.206	0.210	0.206	0.223	0.225	0.221	0.227	0.231	0.224	0.216	0.132	0.183
29	0.193	0.210	0.208	0.197	0.219	0.218	0.173	0.198	0.197	0.186	0.211	0.208	0.198	0.226	0.225	0.202	0.230	0.229	0.193	0.150	0.183
30	0.172	0.169	0.170	0.174	0.180	0.181	0.152	0.150	0.153	0.166	0.178	0.173	0.174	0.185	0.185	0.175	0.190	0.189	0.167	0.109	0.155
31	0.199	0.200	0.201	0.205	0.209	0.210	0.182	0.186	0.185	0.195	0.198	0.195	0.212	0.215	0.215	0.213	0.219	0.217	0.206	0.147	0.183
32*	0.190	0.162	0.164	0.195	0.172	0.175	0.175	0.140	0.144	0.191	0.169	0.162	0.199	0.176	0.177	0.205	0.181	0.180	0.197	0.107	0.155
33	0.207	0.199	0.202	0.214	0.208	0.209	0.193	0.185	0.185	0.210	0.198	0.194	0.218	0.215	0.215	0.226	0.218	0.216	0.218	0.148	0.183
34*	0.188	0.185	0.188	0.192	0.192	0.196	0.169	0.163	0.163	0.179	0.176	0.173	0.196	0.196	0.200	0.196	0.198	0.199	0.189	0.161	0.182
35	0.215	0.216	0.215	0.221	0.224	0.224	0.201	0.202	0.206	0.209	0.210	0.210	0.228	0.232	0.234	0.235	0.234	0.237	0.224	0.164	0.211
36	0.196	0.203	0.202	0.199	0.210	0.213	0.178	0.184	0.189	0.177	0.192	0.193	0.203	0.217	0.223	0.206	0.217	0.224	0.194	0.177	0.210
37*	0.223	0.221	0.222	0.232	0.230	0.229	0.211	0.212	0.216	0.221	0.218	0.218	0.242	0.240	0.238	0.247	0.244	0.242	0.236	0.149	0.211
38	0.212	0.211	0.212	0.217	0.219	0.220	0.193	0.196	0.201	0.204	0.204	0.204	0.220	0.227	0.229	0.226	0.229	0.231	0.214	0.163	0.211
39	0.203	0.211	0.212	0.208	0.220	0.221	0.186	0.197	0.202	0.189	0.204	0.205	0.215	0.228	0.230	0.217	0.229	0.232	0.205	0.163	0.211

40	0.344	0.299	0.292	0.355	0.308	0.308	0.347	0.287	0.284	0.351	0.305	0.302	0.372	0.315	0.317	0.380	0.316	0.319	0.360	0.258	0.238
41		0.322	0.316		0.333	0.328		0.319	0.311		0.332	0.327		0.341	0.338		0.345	0.340		0.256	0.238
42	0.317	0.317	0.313	0.329	0.328	0.324	0.313	0.314	0.306	0.327	0.327	0.322	0.343	0.336	0.333	0.350	0.340	0.335	0.332	0.254	0.238
43		0.293	0.289		0.302	0.303		0.279	0.277		0.298	0.294		0.309	0.312		0.310	0.312		0.256	0.238
44		0.309	0.304		0.317	0.316		0.299	0.292		0.312	0.308		0.324	0.326		0.326	0.325		0.269	0.238
45		0.274	0.269		0.285	0.285		0.259	0.255		0.288	0.281		0.290	0.291		0.293	0.293		0.229	0.210
46*	0.287	0.275	0.269	0.299	0.285	0.285	0.275	0.259	0.256	0.306	0.288	0.282	0.306	0.290	0.292	0.315	0.293	0.293	0.304	0.229	0.210
47	0.301	0.321	0.320	0.313	0.333	0.328	0.297	0.321	0.314	0.308	0.334	0.328	0.326	0.342	0.336	0.335	0.348	0.338	0.315	0.239	0.238
48*	0.287	0.305	0.300	0.298	0.316	0.313	0.272	0.297	0.295	0.298	0.316	0.311	0.304	0.324	0.322	0.313	0.327	0.325	0.298	0.242	0.238
49	0.283	0.312	0.310	0.294	0.322	0.320	0.269	0.307	0.300	0.290	0.320	0.314	0.305	0.330	0.328	0.309	0.334	0.328	0.296	0.254	0.238
50	0.261	0.266	0.262	0.272	0.278	0.278	0.247	0.251	0.252	0.278	0.285	0.278	0.278	0.284	0.283	0.287	0.289	0.287	0.272	0.201	0.210
51*	0.278	0.279	0.276	0.289	0.291	0.289	0.271	0.267	0.264	0.296	0.296	0.288	0.296	0.296	0.294	0.311	0.302	0.297	0.296	0.214	0.210
52		0.289	0.286		0.298	0.300		0.274	0.272		0.293	0.289		0.304	0.307		0.306	0.307		0.255	0.238
53*	0.253	0.255	0.251	0.264	0.265	0.268	0.232	0.234	0.235	0.275	0.268	0.262	0.268	0.269	0.273	0.272	0.272	0.275	0.269	0.215	0.210
54		0.237	0.233		0.249	0.251		0.215	0.215		0.259	0.250		0.251	0.254		0.256	0.257		0.190	0.182
55*	0.328	0.324	0.320	0.341	0.333	0.331	0.326	0.318	0.317	0.349	0.326	0.325	0.356	0.343	0.343	0.363	0.345	0.344	0.347	0.268	0.266
56		0.316	0.315		0.326	0.325		0.308	0.308		0.317	0.315		0.335	0.335		0.336	0.335		0.266	0.266
57		0.314	0.310		0.322	0.323		0.303	0.301		0.311	0.311		0.330	0.334		0.330	0.334		0.282	0.265
58*	0.312	0.301	0.301	0.321	0.308	0.311	0.304	0.285	0.285	0.302	0.294	0.293	0.335	0.314	0.320	0.341	0.314	0.317	0.319	0.279	0.265
59		0.276	0.272		0.285	0.288		0.257	0.260		0.282	0.278		0.291	0.296		0.292	0.297		0.242	0.238
60		0.326	0.325		0.337	0.334		0.324	0.323		0.332	0.330		0.348	0.344		0.351	0.346		0.252	0.266
61		0.329	0.323		0.339	0.336		0.325	0.323		0.333	0.332		0.349	0.348		0.351	0.351		0.270	0.266
62	0.277	0.289	0.285	0.287	0.301	0.300	0.256	0.277	0.279	0.291	0.301	0.297	0.296	0.308	0.308	0.297	0.311	0.312	0.283	0.229	0.238
63		0.316	0.315		0.326	0.325		0.309	0.308		0.317	0.315		0.335	0.335		0.336	0.336		0.266	0.266
64		0.278	0.278		0.289	0.291		0.263	0.267		0.288	0.283		0.296	0.297		0.299	0.299		0.225	0.238
65		0.281	0.276		0.291	0.293		0.264	0.266		0.289	0.285		0.297	0.301		0.298	0.303		0.243	0.238
66*	0.316	0.316	0.318	0.328	0.326	0.325	0.313	0.310	0.311	0.326	0.319	0.316	0.343	0.336	0.333	0.350	0.340	0.334	0.332	0.249	0.266
67	0.294	0.317	0.315	0.303	0.326	0.325	0.279	0.309	0.308	0.294	0.317	0.316	0.312	0.335	0.335	0.318	0.337	0.336	0.301	0.266	0.266
68	0.285	0.299	0.304	0.294	0.308	0.311	0.270	0.287	0.288	0.280	0.296	0.293	0.305	0.315	0.317	0.308	0.317	0.315	0.290	0.262	0.266
69	0.258	0.276	0.276	0.268	0.287	0.289	0.238	0.261	0.264	0.265	0.285	0.281	0.274	0.293	0.295	0.278	0.297	0.296	0.264	0.225	0.238
70		0.308	0.310		0.317	0.319		0.298	0.299		0.307	0.305		0.326	0.327		0.328	0.326		0.264	0.266
71	0.287	0.271	0.273	0.299	0.281	0.284	0.275	0.253	0.257	0.306	0.278	0.273	0.306	0.287	0.289	0.315	0.290	0.290	0.303	0.223	0.238
72	0.274	0.292	0.295	0.281	0.299	0.305	0.253	0.275	0.275	0.261	0.284	0.282	0.289	0.305	0.311	0.291	0.305	0.308	0.277	0.277	0.265
73	0.257	0.255	0.259	0.266	0.263	0.271	0.234	0.230	0.235	0.262	0.255	0.251	0.269	0.267	0.274	0.273	0.269	0.272	0.264	0.236	0.238
74	0.309	0.319	0.320	0.319	0.330	0.328	0.299	0.315	0.315	0.310	0.324	0.321	0.334	0.340	0.337	0.338	0.344	0.338	0.318	0.249	0.266
75	0.278	0.279	0.282	0.290	0.291	0.292	0.271	0.267	0.271	0.296	0.292	0.286	0.296	0.298	0.296	0.311	0.304	0.299	0.296	0.208	0.238
76	0.311	0.300	0.305	0.322	0.309	0.312	0.300	0.288	0.288	0.322	0.296	0.294	0.329	0.316	0.318	0.339	0.318	0.316	0.322	0.262	0.266
77	0.343	0.338	0.336	0.355	0.348	0.346	0.347	0.336	0.340	0.350	0.338	0.340	0.372	0.361	0.359	0.380	0.362	0.362	0.359	0.268	0.294
78	0.325	0.328	0.325	0.334	0.337	0.337	0.318	0.320	0.325	0.322	0.324	0.326	0.346	0.348	0.350	0.354	0.347	0.352	0.333	0.281	0.294
79	0.312	0.329	0.325	0.321	0.338	0.337	0.304	0.321	0.326	0.302	0.325	0.327	0.335	0.349	0.351	0.341	0.348	0.353	0.320	0.281	0.294
80*	0.284	0.317	0.313	0.289	0.324	0.327	0.267	0.303	0.308	0.255	0.308	0.310	0.299	0.333	0.340	0.304	0.331	0.340	0.281	0.293	0.293
81	0.339	0.333	0.333	0.350	0.343	0.342	0.335	0.330	0.334	0.344	0.333	0.334	0.365	0.355	0.354	0.370	0.357	0.357	0.349	0.266	0.294
82		0.453	0.447		0.458	0.454		0.457	0.450		0.459	0.457		0.465	0.464		0.467	0.464		0.443	0.390
83		0.438	0.433		0.442	0.442		0.435	0.429		0.438	0.436		0.447	0.450		0.447	0.448		0.457	0.390

Table 4 (continued)

No	DB-1			DB-5			HT-5			DB-17			DB-XLB			HT-8			CP-Sil 19		
	OBS	M1	MT1	OBS	M2	MT2	OBS	M3	MT3	OBS	M4	MT4	OBS	M5	MT5	OBS	M6	MT6	OBS	M7	MT7
84		0.405	0.400		0.411	0.412		0.397	0.394		0.416	0.411		0.414	0.417		0.415	0.417		0.417	0.362
85*	0.476	0.455	0.452	0.486	0.462	0.457	0.498	0.463	0.456	0.500	0.465	0.462	0.499	0.470	0.465	0.508	0.474	0.466	0.479	0.427	0.391
86	0.452	0.448	0.445	0.462	0.454	0.451	0.455	0.451	0.445	0.478	0.454	0.451	0.466	0.460	0.459	0.475	0.462	0.459	0.453	0.443	0.390
87	0.450	0.446	0.443	0.460	0.451	0.449	0.457	0.448	0.442	0.471	0.451	0.448	0.473	0.458	0.457	0.476	0.460	0.456	0.456	0.442	0.390
88*	0.411	0.396	0.393	0.423	0.404	0.404	0.409	0.388	0.390	0.444	0.412	0.407	0.431	0.407	0.408	0.438	0.411	0.410	0.416	0.389	0.363
89		0.413	0.409		0.420	0.419		0.409	0.406		0.428	0.422		0.424	0.424		0.428	0.425		0.403	0.363
90		0.440	0.439		0.445	0.444		0.441	0.435		0.443	0.440		0.451	0.451		0.453	0.449		0.441	0.390
91		0.408	0.406		0.415	0.415		0.403	0.401		0.422	0.416		0.419	0.419		0.422	0.420		0.401	0.363
92		0.417	0.415		0.421	0.424		0.408	0.407		0.417	0.415		0.425	0.430		0.425	0.428		0.442	0.390
93		0.401	0.398		0.407	0.408		0.391	0.389		0.410	0.405		0.409	0.413		0.411	0.412		0.417	0.362
94		0.398	0.396		0.404	0.406		0.388	0.385		0.407	0.402		0.406	0.410		0.407	0.409		0.416	0.362
95		0.399	0.396		0.405	0.407		0.389	0.387		0.408	0.403		0.407	0.411		0.409	0.410		0.416	0.362
96		0.350	0.347		0.357	0.362		0.329	0.335		0.369	0.362		0.356	0.363		0.360	0.364		0.363	0.334
97*	0.450	0.435	0.431	0.457	0.441	0.439	0.455	0.434	0.432	0.452	0.442	0.440	0.469	0.447	0.447	0.472	0.448	0.448	0.446	0.430	0.390
98	0.405	0.409	0.406	0.414	0.416	0.415	0.400	0.404	0.402	0.414	0.423	0.417	0.423	0.420	0.420	0.428	0.423	0.421	0.403	0.402	0.363
99	0.425	0.444	0.441	0.433	0.452	0.448	0.424	0.449	0.447	0.430	0.457	0.454	0.443	0.460	0.456	0.447	0.463	0.459	0.422	0.415	0.391
100	0.395	0.429	0.426	0.405	0.438	0.433	0.396	0.433	0.428	0.403	0.449	0.443	0.413	0.444	0.438	0.424	0.450	0.442	0.394	0.394	0.363
101	0.401	0.431	0.428	0.410	0.436	0.436	0.389	0.428	0.427	0.403	0.437	0.434	0.418	0.442	0.443	0.418	0.444	0.443	0.400	0.429	0.390
102	0.385	0.397	0.394	0.396	0.405	0.405	0.370	0.389	0.391	0.408	0.413	0.408	0.396	0.408	0.409	0.404	0.412	0.412	0.389	0.389	0.363
103*	0.358	0.427	0.414	0.369	0.436	0.430	0.336	0.428	0.426	0.372	0.450	0.447	0.374	0.442	0.440	0.373	0.445	0.447	0.360	0.398	0.363
104*	0.357	0.360	0.357	0.369	0.369	0.372	0.344	0.345	0.351	0.383	0.385	0.377	0.373	0.371	0.372	0.382	0.376	0.376	0.359	0.349	0.335
105*	0.496	0.463	0.460	0.506	0.469	0.465	0.519	0.469	0.469	0.519	0.467	0.467	0.519	0.479	0.476	0.524	0.480	0.477	0.500	0.441	0.419
106*	0.461	0.464	0.457	0.469	0.469	0.466	0.464	0.468	0.466	0.472	0.466	0.467	0.477	0.478	0.478	0.481	0.478	0.480	0.457	0.459	0.418
107		0.453	0.450		0.458	0.457		0.454	0.453		0.452	0.452		0.465	0.467		0.465	0.467		0.456	0.418
108*	0.451	0.446	0.445	0.461	0.450	0.451	0.456	0.444	0.445	0.460	0.443	0.443	0.473	0.457	0.459	0.474	0.457	0.458	0.450	0.454	0.418
109	0.406	0.424	0.418	0.417	0.430	0.429	0.395	0.420	0.422	0.427	0.434	0.432	0.427	0.436	0.438	0.425	0.438	0.440	0.407	0.417	0.390
110		0.415	0.413		0.421	0.422		0.409	0.412		0.423	0.420		0.427	0.429		0.428	0.430		0.415	0.390
111		0.436	0.435		0.439	0.442		0.429	0.429		0.427	0.428		0.444	0.450		0.442	0.447		0.468	0.418
112		0.416	0.409		0.421	0.422		0.407	0.409		0.421	0.420		0.425	0.431		0.425	0.431		0.432	0.390
113		0.399	0.398		0.403	0.408		0.384	0.389		0.399	0.397		0.406	0.413		0.406	0.411		0.428	0.390
114	0.483	0.466	0.462	0.491	0.472	0.468	0.494	0.473	0.472	0.495	0.471	0.471	0.503	0.482	0.479	0.505	0.484	0.481	0.478	0.442	0.419
115	0.434	0.426	0.424	0.442	0.434	0.432	0.435	0.425	0.429	0.445	0.439	0.437	0.457	0.441	0.439	0.458	0.444	0.442	0.430	0.401	0.391
116*	0.434	0.432	0.424	0.444	0.439	0.436	0.424	0.430	0.432	0.463	0.443	0.442	0.454	0.445	0.446	0.452	0.447	0.450	0.430	0.420	0.390
117		0.418	0.415		0.425	0.425		0.413	0.416		0.427	0.425		0.430	0.432		0.432	0.434		0.416	0.390
118	0.450	0.455	0.455	0.457	0.461	0.459	0.455	0.459	0.459	0.452	0.457	0.456	0.469	0.469	0.467	0.472	0.471	0.468	0.447	0.439	0.419
119*	0.405	0.415	0.416	0.414	0.422	0.422	0.400	0.411	0.415	0.416	0.425	0.422	0.423	0.428	0.427	0.428	0.432	0.429	0.403	0.398	0.391
120*	0.408	0.437	0.439	0.414	0.441	0.443	0.398	0.433	0.434	0.394	0.432	0.432	0.423	0.447	0.450	0.424	0.448	0.448	0.400	0.451	0.418
121	0.363	0.398	0.401	0.371	0.403	0.408	0.339	0.386	0.391	0.362	0.401	0.397	0.377	0.407	0.411	0.375	0.409	0.409	0.356	0.410	0.390
122		0.443	0.444		0.448	0.449		0.441	0.441		0.439	0.439		0.454	0.457		0.454	0.455		0.453	0.418
123	0.453	0.441	0.446	0.462	0.447	0.448	0.459	0.442	0.443	0.462	0.440	0.439	0.471	0.454	0.453	0.476	0.456	0.452	0.449	0.436	0.419

124	0.436	0.434	0.438	0.443	0.438	0.441	0.432	0.430	0.431	0.435	0.428	0.428	0.453	0.444	0.447	0.454	0.444	0.444	0.432	0.451	0.451	0.418
125	0.414	0.397	0.401	0.424	0.403	0.407	0.403	0.386	0.391	0.436	0.400	0.397	0.426	0.406	0.410	0.431	0.408	0.409	0.415	0.411	0.411	0.390
126	0.490	0.478	0.472	0.495	0.483	0.479	0.507	0.485	0.489	0.489	0.477	0.481	0.508	0.495	0.494	0.513	0.495	0.497	0.485	0.458	0.458	0.447
127	0.449	0.469	0.462	0.454	0.473	0.472	0.453	0.471	0.475	0.430	0.465	0.469	0.465	0.484	0.486	0.469	0.481	0.488	0.439	0.471	0.471	0.446
128	0.679	0.601	0.595	0.677	0.601	0.595	0.730	0.617	0.615	0.702	0.610	0.610	0.680	0.605	0.602	0.682	0.607	0.605	0.704	0.659	0.659	0.613
129		0.598	0.594		0.595	0.592		0.610	0.604		0.598	0.598		0.597	0.598		0.597	0.597		0.684	0.684	0.612
130		0.594	0.591		0.591	0.589		0.606	0.600		0.593	0.594		0.593	0.594		0.593	0.592		0.683	0.683	0.612
131*	0.586	0.563	0.558	0.586	0.562	0.560	0.598	0.569	0.567	0.595	0.573	0.571	0.590	0.562	0.563	0.586	0.564	0.564	0.562	0.644	0.644	0.585
132		0.562	0.558		0.561	0.560		0.568	0.566		0.572	0.570		0.561	0.562		0.563	0.563			0.644	0.644	0.585
133		0.565	0.563		0.560	0.563		0.564	0.564		0.558	0.559		0.559	0.566		0.557	0.562			0.684	0.684	0.612
134		0.551	0.547		0.548	0.550		0.551	0.549		0.555	0.553		0.546	0.552		0.546	0.550			0.658	0.658	0.584
135		0.530	0.529		0.527	0.532		0.524	0.527		0.533	0.531		0.524	0.532		0.524	0.530			0.644	0.644	0.584
136		0.517	0.512		0.515	0.518		0.510	0.512		0.530	0.526		0.511	0.517		0.513	0.518			0.618	0.618	0.556
137		0.599	0.599		0.598	0.594		0.615	0.610		0.602	0.602		0.601	0.598		0.603	0.597			0.668	0.668	0.613
138*	0.618	0.595	0.591	0.617	0.594	0.590	0.644	0.610	0.608	0.626	0.602	0.602	0.619	0.598	0.595	0.620	0.600	0.597	0.605	0.657	0.657	0.613
139	0.576	0.555	0.553	0.577	0.556	0.554	0.595	0.562	0.564	0.610	0.570	0.567	0.579	0.557	0.555	0.584	0.560	0.558	0.551	0.616	0.616	0.585
140	0.586	0.565	0.564	0.588	0.565	0.563	0.614	0.575	0.573	0.603	0.578	0.575	0.588	0.566	0.563	0.597	0.570	0.565	0.565	0.628	0.628	0.585
141	0.587	0.581	0.578	0.585	0.578	0.577	0.594	0.588	0.587	0.588	0.581	0.582	0.586	0.580	0.582	0.582	0.580	0.581	0.563	0.671	0.671	0.612
142	0.595	0.546	0.543	0.598	0.545	0.545	0.610	0.547	0.549	0.624	0.555	0.553	0.597	0.544	0.546	0.599	0.545	0.547	0.578	0.631	0.631	0.585
143		0.549	0.545		0.548	0.548		0.551	0.553		0.560	0.558		0.548	0.550		0.549	0.552			0.632	0.632	0.585
144	0.528	0.541	0.540	0.531	0.540	0.541	0.516	0.541	0.544	0.543	0.549	0.547	0.533	0.538	0.542	0.524	0.540	0.542	0.507	0.630	0.630	0.585
145		0.510	0.507		0.511	0.513		0.504	0.511		0.529	0.524		0.508	0.511		0.511	0.514			0.591	0.591	0.557
146		0.586	0.586		0.583	0.582		0.595	0.590		0.583	0.582		0.584	0.585		0.584	0.582			0.682	0.682	0.612
147		0.553	0.552		0.551	0.552		0.556	0.554		0.559	0.556		0.550	0.552		0.552	0.551			0.642	0.642	0.585
148		0.550	0.551		0.549	0.550		0.553	0.552		0.556	0.553		0.547	0.549		0.549	0.548			0.641	0.641	0.585
149		0.543	0.541		0.541	0.543		0.543	0.546		0.552	0.549		0.540	0.543		0.542	0.544			0.630	0.630	0.585
150		0.508	0.506		0.508	0.511		0.501	0.508		0.526	0.521		0.505	0.508		0.508	0.511			0.590	0.590	0.557
151		0.526	0.526		0.523	0.528		0.519	0.522		0.528	0.526		0.520	0.528		0.520	0.525			0.643	0.643	0.584
152		0.496	0.494		0.494	0.500		0.483	0.490		0.508	0.504		0.489	0.497		0.491	0.497			0.604	0.604	0.556
153	0.563	0.591	0.588	0.560	0.590	0.587	0.564	0.605	0.603	0.552	0.597	0.597	0.560	0.594	0.591	0.558	0.595	0.593	0.531	0.656	0.656	0.613
154	0.515	0.558	0.560	0.517	0.557	0.557	0.504	0.565	0.564	0.518	0.568	0.564	0.513	0.557	0.555	0.513	0.561	0.556	0.487	0.627	0.627	0.585
155	0.491	0.523	0.525	0.496	0.525	0.525	0.483	0.525	0.527	0.500	0.544	0.537	0.494	0.523	0.521	0.497	0.529	0.524	0.462	0.587	0.587	0.557
156	0.644	0.623	0.616	0.640	0.621	0.615	0.672	0.641	0.640	0.643	0.624	0.627	0.642	0.627	0.625	0.640	0.627	0.627	0.637	0.685	0.685	0.641
157		0.608	0.607		0.606	0.603		0.623	0.623		0.606	0.609		0.611	0.610		0.611	0.610		0.682	0.682	0.641
158	0.586	0.582	0.577	0.587	0.582	0.579	0.598	0.593	0.596	0.597	0.592	0.592	0.590	0.586	0.584	0.586	0.587	0.588	0.563	0.644	0.644	0.613
159*	0.593	0.605	0.600	0.590	0.601	0.599	0.603	0.615	0.615	0.578	0.598	0.602	0.591	0.604	0.607	0.587	0.602	0.606	0.564	0.698	0.698	0.640
160	0.589	0.586	0.576	0.590	0.585	0.581	0.592	0.595	0.597	0.609	0.593	0.595	0.592	0.588	0.589	0.584	0.587	0.593	0.567	0.662	0.662	0.612
161	0.533	0.565	0.562	0.535	0.562	0.563	0.521	0.568	0.572	0.534	0.567	0.568	0.536	0.563	0.567	0.526	0.563	0.567	0.505	0.657	0.657	0.612
162		0.598	0.596		0.594	0.594		0.607	0.607		0.590	0.594		0.597	0.601		0.596	0.599			0.696	0.696	0.640
163		0.575	0.568		0.573	0.571		0.580	0.583		0.579	0.580		0.575	0.577		0.574	0.579			0.659	0.659	0.612
164		0.561	0.560		0.559	0.561		0.563	0.567		0.562	0.563		0.559	0.564		0.559	0.563			0.656	0.656	0.612
165		0.557	0.553		0.553	0.556		0.555	0.559		0.554	0.556		0.553	0.561		0.551	0.559			0.672	0.672	0.612
166	0.623	0.588	0.581	0.621	0.588	0.583	0.643	0.601	0.603	0.631	0.599	0.600	0.627	0.592	0.590	0.622	0.594	0.595	0.603	0.646	0.646	0.613
167*	0.600	0.599	0.601	0.596	0.596	0.596	0.613	0.611	0.612	0.588	0.594	0.597	0.596	0.600	0.600	0.594	0.601	0.599	0.572	0.679	0.679	0.641

Table 4 (continued)

No	DB-1			DB-5			HT-5			DB-17			DB-XLB			HT-8			CP-Sil 19		
	OBS	M1	MT1	OBS	M2	MT2	OBS	M3	MT3	OBS	M4	MT4	OBS	M5	MT5	OBS	M6	MT6	OBS	M7	MT7
168*	0.547	0.559	0.563	0.548	0.558	0.560	0.543	0.564	0.569	0.551	0.563	0.562	0.545	0.559	0.560	0.543	0.562	0.560	0.515	0.638	0.613
169		0.638	0.628		0.636	0.629		0.657	0.661		0.635	0.643		0.644	0.643		0.642	0.647		0.701	0.669
170		0.769	0.766		0.756	0.751		0.797	0.792		0.766	0.769		0.754	0.751		0.754	0.751		0.952	0.904
171		0.723	0.719		0.712	0.709		0.742	0.744		0.731	0.733		0.707	0.707		0.709	0.710		0.900	0.877
172		0.754	0.753		0.740	0.738		0.776	0.771		0.745	0.749		0.735	0.738		0.734	0.735		0.965	0.904
173	0.779	0.710	0.707	0.763	0.698	0.698	0.807	0.722	0.725	0.776	0.712	0.714	0.755	0.691	0.695	0.743	0.691	0.695	0.850	0.914	0.876
174		0.709	0.706		0.697	0.698		0.722	0.725		0.712	0.713		0.690	0.694		0.690	0.695		0.914	0.876
175		0.719	0.717		0.707	0.706		0.735	0.734		0.719	0.721		0.700	0.703		0.700	0.702		0.925	0.876
176		0.689	0.685		0.678	0.678		0.699	0.701		0.700	0.698		0.669	0.673		0.671	0.674		0.886	0.848
177		0.722	0.719		0.710	0.709		0.738	0.737		0.723	0.724		0.703	0.706		0.703	0.705		0.926	0.876
178		0.688	0.689		0.674	0.679		0.692	0.696		0.682	0.684		0.664	0.674		0.662	0.670		0.926	0.876
179		0.657	0.656		0.644	0.650		0.655	0.662		0.661	0.660		0.633	0.643		0.632	0.641		0.887	0.848
180		0.756	0.753		0.744	0.740		0.781	0.780		0.755	0.759		0.741	0.740		0.741	0.741		0.940	0.904
181*	0.770	0.727	0.727	0.754	0.716	0.714	0.807	0.748	0.747	0.761	0.732	0.732	0.744	0.711	0.710	0.742	0.713	0.710	0.823	0.911	0.877
182	0.707	0.724	0.725	0.697	0.713	0.711	0.717	0.744	0.743	0.708	0.728	0.728	0.680	0.707	0.707	0.675	0.709	0.707	0.696	0.910	0.877
183*	0.699	0.717	0.715	0.687	0.706	0.704	0.703	0.734	0.737	0.692	0.724	0.725	0.674	0.700	0.701	0.665	0.702	0.703	0.685	0.899	0.877
184	0.673	0.683	0.680	0.666	0.674	0.673	0.683	0.694	0.701	0.679	0.700	0.698	0.654	0.666	0.667	0.652	0.670	0.671	0.636	0.859	0.849
185*	0.713	0.704	0.703	0.702	0.692	0.693	0.716	0.715	0.718	0.714	0.705	0.706	0.693	0.684	0.689	0.676	0.684	0.688	0.722	0.913	0.876
186		0.674	0.671		0.664	0.666		0.680	0.687		0.686	0.685		0.655	0.659		0.656	0.662		0.874	0.848
187		0.701	0.701		0.689	0.691		0.712	0.715		0.702	0.703		0.681	0.686		0.681	0.685		0.912	0.876
188		0.668	0.667		0.657	0.660		0.672	0.679		0.678	0.677		0.647	0.653		0.649	0.654		0.872	0.848
189		0.782	0.777		0.769	0.764		0.811	0.811		0.775	0.782		0.769	0.768		0.767	0.769		0.967	0.932
190	0.780	0.737	0.735	0.763	0.725	0.723	0.807	0.756	0.761	0.778	0.736	0.740	0.755	0.721	0.722	0.742	0.721	0.724	0.852	0.925	0.904
191	0.734	0.742	0.739	0.721	0.731	0.728	0.744	0.764	0.767	0.729	0.743	0.748	0.708	0.728	0.728	0.695	0.728	0.731	0.746	0.926	0.904
192	0.721	0.742	0.734	0.707	0.729	0.727	0.720	0.760	0.763	0.710	0.739	0.745	0.698	0.725	0.729	0.678	0.723	0.730	0.722	0.943	0.904
193		0.735	0.730		0.722	0.721		0.751	0.754		0.731	0.736		0.717	0.722		0.715	0.722		0.941	0.904
194		0.933	0.929		0.908	0.903		0.972	0.971		0.923	0.931		0.897	0.898		0.895	0.899		1.256	1.265
195		0.909	0.905		0.885	0.880		0.944	0.943		0.906	0.911		0.872	0.872		0.872	0.874		1.228	1.238
196		0.895	0.892		0.871	0.868		0.927	0.930		0.894	0.900		0.858	0.860		0.858	0.862		1.215	1.238
197		0.859	0.856		0.837	0.835		0.884	0.890		0.867	0.870		0.821	0.823		0.823	0.828		1.175	1.210
198	0.882	0.895	0.892	0.853	0.869	0.868	0.899	0.923	0.922	0.860	0.886	0.891	0.828	0.854	0.859	0.809	0.852	0.858	1.094	1.241	1.237
199		0.879	0.877		0.853	0.854		0.903	0.906		0.871	0.876		0.838	0.844		0.836	0.844		1.228	1.237
200		0.847	0.844		0.823	0.825		0.866	0.873		0.850	0.853		0.806	0.813		0.806	0.814		1.189	1.209
201		0.843	0.842		0.819	0.822		0.860	0.868		0.844	0.847		0.801	0.808		0.801	0.809		1.188	1.209
202		0.827	0.828		0.801	0.808		0.837	0.845		0.821	0.824		0.781	0.793		0.779	0.791		1.201	1.209
203	0.885	0.900	0.900	0.855	0.876	0.873	0.903	0.934	0.933	0.859	0.896	0.900	0.830	0.862	0.863	0.812	0.863	0.863	1.100	1.227	1.238
204*	0.858	0.858	0.855	0.834	0.836	0.835	0.885	0.883	0.890	0.849	0.866	0.869	0.810	0.821	0.823	0.801	0.822	0.827	0.981	1.175	1.210
205*	0.922	0.931	0.922	0.891	0.907	0.901	0.944	0.970	0.972	0.904	0.927	0.936	0.865	0.898	0.898	0.842	0.895	0.903	1.254	1.245	1.265
206*	1.074	1.078	1.075	1.027	1.039	1.036	1.111	1.124	1.127	1.048	1.067	1.077	0.997	1.017	1.020	1.009	1.015	1.023	2.091	1.557	1.668
207	1.042	1.043	1.040	1.001	1.006	1.004	1.089	1.082	1.089	1.024	1.042	1.049	0.965	0.982	0.985	0.972	0.982	0.990	1.741	1.517	1.640
208	1.029	1.027	1.025	0.988	0.988	0.990	1.073	1.059	1.066	1.004	1.018	1.026	0.955	0.961	0.970	0.939	0.959	0.971	1.661	1.530	1.640
209	1.219	1.235	1.231	1.171	1.181	1.179	1.290	1.290	1.297	1.282	1.223	1.235	1.196	1.147	1.152	1.281	1.145	1.157	>2.54	1.881	2.140

*refers to the sample in the test set

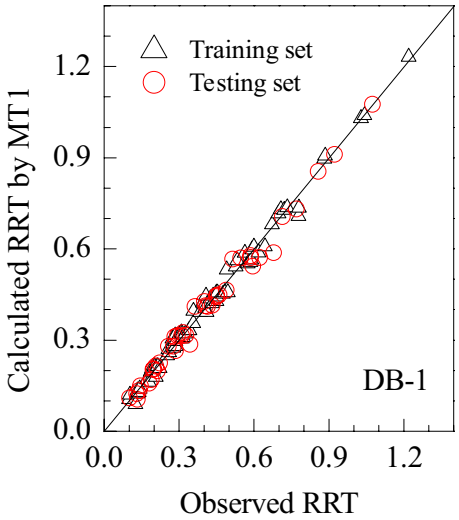

Fig. 2 Plot of RRT calculated by MT1 model versus observed

The *RRT* values calculated using Eq. 2 (MT1 model) are listed in Table 4 together with the GC-*RRT*s observed. The relationship graph between the *RRT* calculated by the MT1 model and observed is shown in Fig. 2 and the distribution of their residual errors shown in Fig. 3. These evidently reveal the fact that E_{HOMO}, the number of bromine atoms in different substituent position and molecular weight ($\ln M_w$) are the most important factors affecting the RRT values. From Table 4 and Fig. 3, only 5 PBDEs (nos. 43, 21, 35, 78, and 37) have high residual errors of >0.05, which explains the model MT1 having indeed a high estimation quality.

Predicting RRT of PBDEs on the other columns

With the help of VSMP program, six optimal QSRR of PBDEs on the other six stationary phases, columns of DB-5, DB-17, DB-XLB, HT-5, HT-8, and CP-Sil 19, were developed by the same way as DB-1 column. The VSMP results show that the best variable subsets for all stationary phases but the CP-Sil 19 column are the combination consisting of six descriptors of nos. 3, 11, 12, 13, 14, and 15, which indicates that the factors expressed by the six descriptors, $\ln M_W$, E^2_{HOMO}, E^2_{LUMO}, *o*-Br, *m*-Br, and *p*-Br, are the most important structural features affecting the GC-RRT values of PBDEs. However, for the CP-Sil 19 column, main factors related closely to the RRT values are four descriptors of nos. 13, 14, 15, and 16, i.e., *o*-Br, *m*-Br, *p*-Br, and $Br^{1/2}$. Except for the model (noted M7) from the CP-Sil 19 column (Eq. 8), the other five QSRR models (Eqs. 3–7 corresponding to model M2, M3, M4, M5, and M6, respectively) have good calibrated abilities of r>0.99 and high stabilities of q>0.99.

These models (M2~M7) and some statistics are as follow. For DB-5 column (M2),

$$\begin{aligned} RRT =& (4.8376 \pm 0.2931) - (0.8772 \pm 0.0513)\ \cdot \boldsymbol{x_3} \\ & -(0.002215 \pm 0.000319)\ \cdot \boldsymbol{x_{11}} - (0.05056 \\ & \pm 0.01093)\ \cdot \boldsymbol{x_{12}} + (0.2440 \pm 0.0103)\ \cdot \boldsymbol{x_{13}} \\ & +(0.2850\ \pm 0.0115)\ \cdot \boldsymbol{x_{14}} \\ & +(0.2937 \pm 0.0118)\ \cdot \boldsymbol{x_{15}} \end{aligned} \tag{3}$$

$n = 126,\ m = 6,\ r^2 = 0.9917,\ r = 0.9958,$
$RMSE = 0.020,\ F = 2359.7$ (Estimation)
$n = 126,\ m = 6,\ q^2 = 0.9904,\ \mathrm{q} = 0.9952,$
$RMSV = 0.022$ (LOO validation).

For HT-5 column (M3),

$$\begin{aligned} RRT =& (6.6890 \pm 0.4030) - (1.2146 \pm 0.0705)\ \cdot \boldsymbol{x_3} \\ & -(0.002820 \pm 0.000425)\ \cdot \boldsymbol{x_{11}} \\ & -(0.06216 \pm 0.01503)\ \cdot \boldsymbol{x_{12}} \\ & +(0.3032 \pm 0.0141)\ \cdot \boldsymbol{x_{13}} \\ & +(0.3539\ \pm 0.0158)\ \cdot \boldsymbol{x_{14}} \\ & +(0.3661 \pm 0.0162)\ \cdot \boldsymbol{x_{15}} \end{aligned} \tag{4}$$

$n = 126,\ m = 6,\ r^2 = 0.9871,\ r = 0.9936,$
$RMSE = 0.028,\ F = 1523.0$ (Estimation)
$n = 126,\ m = 6,\ q^2 = 0.9855,\ q = 0.9927,$
$RMSV = 0.030$ (LOO validation).

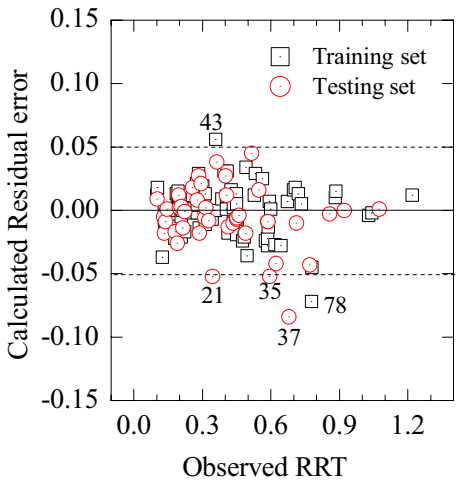

Fig. 3 Distribution of the residual errors between the RRT calculated using MT1 model and observed

For DB-17 column (M4),

$$\begin{aligned} RRT =&(5.3293 \pm 0.3729) - (0.9695 \pm 0.0652)\ \cdot \boldsymbol{x_3} \\ &-(0.002375 \pm 0.000393)\ \cdot \boldsymbol{x_{11}} \\ &-(0.06208 \pm 0.01391)\ \cdot \boldsymbol{x_{12}} \\ &+(0.2709 \pm 0.0130)\ \cdot \boldsymbol{x_{13}} \\ &+(0.3057\ \pm 0.0146)\ \cdot \boldsymbol{x_{14}} \\ &+(0.3175 \pm 0.0150)\ \cdot \boldsymbol{x_{15}} \end{aligned} \quad (5)$$

$n = 126,\ m = 6,\ r^2 = 0.9877,\ r = 0.9938,$
$RMSE = 0.026,\ F = 1591.7$ (Estimation)
$n = 126,\ m = 6,\ q^2 = 0.9867,\ q = 0.9933,$
$RMSV = 0.027$ (LOO validation)

.

For DB-XLB column (M5),

$$\begin{aligned} RRT =&(4.2119 \pm 0.3177) - (0.7612 \pm 0.0556)\ \cdot \boldsymbol{x_3} \\ &-(0.002358 \pm 0.000335)\ \cdot \boldsymbol{x_{11}} \\ &-(0.05564 \pm 0.01185)\ \cdot \boldsymbol{x_{12}} \\ &+(0.2244 \pm 0.0111)\ \cdot \boldsymbol{x_{13}} \\ &+(0.2683\ \pm 0.0125)\ \cdot \boldsymbol{x_{14}} \\ &+(0.2784 \pm 0.0128)\ \cdot \boldsymbol{x_{15}} \end{aligned} \quad (6)$$

$n = 126,\ m = 6,\ r^2 = 0.9898,\ r = 0.9949,$
$RMSE = 0.022,\ F = 1931.5$ (Estimation)
$n = 126,\ m = 6,\ q^2 = 0.9890,\ q = 0.9945,$
$RMSV = 0.023$ (LOO validation)

.

For HT-8 column (M6),

$$\begin{aligned} RRT =&(4.1932 \pm 0.3795) - (0.7570 \pm 0.0664)\ \cdot \boldsymbol{x_3} \\ &-(0.002339 \pm 0.000400)\ \cdot \boldsymbol{x_{11}} \\ &-(0.05432 \pm 0.01415)\ \cdot \boldsymbol{x_{12}} \\ &+(0.2233 \pm 0.0133)\ \cdot \boldsymbol{x_{13}} \\ &+(0.2653\ \pm 0.0149)\ \cdot \boldsymbol{x_{14}} \\ &+(0.2774 \pm 0.0153)\ \cdot \boldsymbol{x_{15}} \end{aligned} \quad (7)$$

$n = 126,\ m = 6,\ r^2 = 0.9854,\ r = 0.9927,$
$RMSE = 0.026,\ F = 1338.2$ (Estimation)
$n = 126,\ m = 6,\ q^2 = 0.9851,\ q = 0.9925,$
$RMSV = 0.027$ (LOO validation)

.

For CP-Sil 19 column (M7),

$$\begin{aligned} RRT =&(0.3646 \pm 0.0455) - (0.1798 \pm 0.0204)\ \cdot \boldsymbol{x_{13}} \\ &-(0.1540 \pm 0.0202)\ \cdot \boldsymbol{x_{14}} \\ &-(0.1558 \pm 0.0205)\ \cdot \boldsymbol{x_{15}} \\ &+(0.03418 \pm 0.00185)\ \cdot \boldsymbol{x_{16}} \end{aligned} \quad (8)$$

$n = 126,\ m = 4,\ r^2 = 0.9392,\ r = 0.9691,$
$RMSE = 0.089,\ F = 467.3$ (Estimation)
$n = 126,\ m = 4,\ q^2 = 0.9345,\ q = 0.9667,$
$RMSV = 0.093$ (LOO validation)

.

From the above results, the model for CP-Sil 19 column (M7) is different from the others six. The possible reason is that the filler of CP-Sil 19 column (14% cyanopropylmethylpolysiloxane) is different from the other columns. In the CP-Sil 19 column, it contains a cyanopropyl group in which the substructure "C≡N" expresses a high polarity. The use of more polar columns will result in unacceptably long analysis times, which will also increase the risk of degradation of higher brominated congeners [11]. It is obvious that the observed RRTs of PBDEs of nos.198 to 209 have higher values than the others columns in Tables 1 and 4.

To examine the applicability of the models, 84 PBDEs are picked up from the 126-PBDE set as a training set and the other 42 as a test set. For six different stationary phases, there are six training sets and six test sets. The 84-PBDEs in the training set are employed to develop a QSRR model which is then used to predict the RRT values of PBDEs in the test set. The RRT values estimated (for the training set) and predicted (for the test set) by these QSRR models developed from the training sets are listed in Table 4 together with the RRTs observed experimentally. The overall relationship profiles between the RRTs calculated by the models and observed are shown in Fig. 4.

These models (MT2~MT7 corresponding to Eqs. 9~ 14) from the six training sets and some statistics are as follows.

For DB-5 column (MT2),

$$\begin{aligned} \mathrm{RRT} =&(4.5567 \pm 0.3785) - (0.8296 \pm 0.0661)\ \cdot \boldsymbol{x_3} \\ &-(0.001860 \pm 0.000387)\ \cdot \boldsymbol{x_{11}} \\ &-(0.03981 \pm 0.01406)\ \cdot \boldsymbol{x_{12}} \\ &+(0.2349 \pm 0.0132)\ \cdot \boldsymbol{x_{13}} \\ &+(0.2729 \pm 0.0151)\ \cdot \boldsymbol{x_{14}} \\ &+(0.2795 \pm 0.0151)\ \cdot \boldsymbol{x_{15}} \end{aligned} \quad (9)$$

$n = 84,\ m = 6,\ r^2 = 0.9917,\ r = 0.9958,$
$RMSE = 0.020,\ F = 1532.6$ (Estimation)
$n = 84,\ m = 6,\ q^2 = 0.9896,\ \mathrm{q} = 0.9948,$
$RMSV = 0.023$ (LOO validation)
$n_t = 42,\ u^2 = 0.9914,\ u = 0.9957,$
$RMSP = 0.021$ (Test prediction)

.

For HT-5 column (MT3),

$$\begin{aligned}\mathrm{RRT} =&(6.5729 \pm 0.5370) - (1.1993 \pm 0.0940) \cdot \boldsymbol{x_3}\\ &-(0.002354 \pm 0.000564) \cdot \boldsymbol{x_{11}}\\ &-(0.05790 \pm 0.01947) \cdot \boldsymbol{x_{12}}\\ &+(0.3030 \pm 0.0188) \cdot \boldsymbol{x_{13}}\\ &+(0.3493 \pm 0.0210) \cdot \boldsymbol{x_{14}}\\ &+(0.3616 \pm 0.0213) \cdot \boldsymbol{x_{15}}\end{aligned}$$

$n = 84,\ m = 6,\ r^2 = 0.9854,\ r = 0.9927,$
$RMSE = 0.030,\ F = 866.2$ (Estimation)
$n = 84,\ m = 6,\ q^2 = 0.9821,\ q = 0.9910,$
$RMSV = 0.034$ (LOO validation)
$n_t = 42,\ u^2 = 0.9904,\ u = 0.9952,$
$RMSP = 0.024$ (Test prediction)

(10)

. For DB-17 column (MT4),

$$\begin{aligned}\mathrm{RRT} =&(5.6218 \pm 0.4939) - (1.0231 \pm 0.0864) \cdot \boldsymbol{x_3}\\ &-(0.002414 \pm 0.000515) \cdot \boldsymbol{x_{11}}\\ &-(0.06504 \pm 0.01807) \cdot \boldsymbol{x_{12}}\\ &+(0.2794 \pm 0.0172) \cdot \boldsymbol{x_{13}}\\ &+(0.3172 \pm 0.0195) \cdot \boldsymbol{x_{14}}\\ &+(0.3283 \pm 0.0200) \cdot \boldsymbol{x_{15}}\end{aligned}$$

$n = 84,\ m = 6,\ r^2 = 0.9866,\ r = 0.9933,$
$RMSE = 0.027,\ F = 942.6$ (Estimation)
$n = 84,\ m = 6,\ q^2 = 0.9846,\ q = 0.9922,$
$RMSV = 0.030$ (LOO validation)
$n_t = 42,\ u^2 = 0.9903,\ u = 0.9951,$
$RMSP = 0.024$ (Test prediction)

(11)

.

For DB-XLB column (MT5),

$$\begin{aligned}\mathrm{RRT} =&(4.1423 \pm 0.4095) - (0.7509 \pm 0.0717) \cdot \boldsymbol{x_3}\\ &-(0.002133 \pm 0.000424) \cdot \boldsymbol{x_{11}}\\ &-(0.05078 \pm 0.01533) \cdot \boldsymbol{x_{12}}\\ &+(0.2230 \pm 0.0144) \cdot \boldsymbol{x_{13}}\\ &+(0.2657 \pm 0.0160) \cdot \boldsymbol{x_{14}}\\ &+(0.2717 \pm 0.0163) \cdot \boldsymbol{x_{15}}\end{aligned}$$

(12)

$n = 84,\ m = 6,\ r^2 = 0.9885,\ r = 0.9942,$
$RMSE = 0.024,\ F = 1102.8$ (Estimation)
$n = 84,\ m = 6,\ q^2 = 0.9871,\ q = 0.9935,$
$RMSV = 0.025$ (LOO validation)
$n_t = 42,\ u^2 = 0.9922,\ u = 0.9961,$
$RMSP = 0.019$ (Test prediction)

.

For HT-8 column (MT6),

$$\begin{aligned}\mathrm{RRT} =&(4.4532 \pm 0.4947) - (0.8058 \pm 0.0864) \cdot \boldsymbol{x_3}\\ &-(0.002231 \pm 0.000542) \cdot \boldsymbol{x_{11}}\\ &-(0.05875 \pm 0.01772) \cdot \boldsymbol{x_{12}}\\ &+(0.2339 \pm 0.0171) \cdot \boldsymbol{x_{13}}\\ &+(0.2758 \pm 0.0192) \cdot \boldsymbol{x_{14}}\\ &+(0.2836 \pm 0.0196) \cdot \boldsymbol{x_{15}}\end{aligned}$$

$n = 84,\ m = 6,\ r^2 = 0.9842,\ r = 0.9921,$
$RMSE = 0.028,\ F = 799.3$ (Estimation)
$n = 84,\ m = 6,\ q^2 = 0.9838,\ q = 0.9918,$
$RMSV = 0.028$ (LOO validation)
$n_t = 42,\ u^2 = 0.9871,\ u = 0.9935,$
$RMSP = 0.024$ (Test prediction)

(13)

.

For CP-Sil 19 column (MT7),

$$\begin{aligned}\mathrm{RRT} =&(0.3788 \pm 0.05230) - (0.1883 \pm 0.0240) \cdot \boldsymbol{x_{13}}\\ &-(0.1605 \pm 0.0233) \cdot \boldsymbol{x_{14}}\\ &-(0.1600 \pm 0.0228) \cdot \boldsymbol{x_{15}}\\ &+(0.03477 \pm 0.00209) \cdot \boldsymbol{x_{16}}\end{aligned}$$

(14)

$n = 84,\ m = 4,\ r^2 = 0.9494,\ r = 0.9743,$
$RMSE = 0.083,\ F = 370.2$ (Estimation)
$n = 84,\ m = 4,\ q^2 = 0.9477,\ q = 0.9735,$
$RMSV = 0.084$ (LOO validation)
$n_t = 42,\ u^2 = 0.9164,\ u = 0.9573,$
$RMSP = 0.101$ (Test prediction)

The results of Eqs. 9–14 and Fig. 4 show that the models, MT2 to MT7 derived from the training sets, have not only high estimation abilities (high r and low $RMSE$) but also good predictive potentials (high u and low $RMSP$). However, the correlation coefficient (r) and the LOO cross validation correlation coefficient (q) for CP-Sil 19 column (r^2=0.949, q^2=0.948) is worse than the other stationary phases (r^2=0.984~0.993, q^2=0.984~0.991) due to the introduction of some polar group.

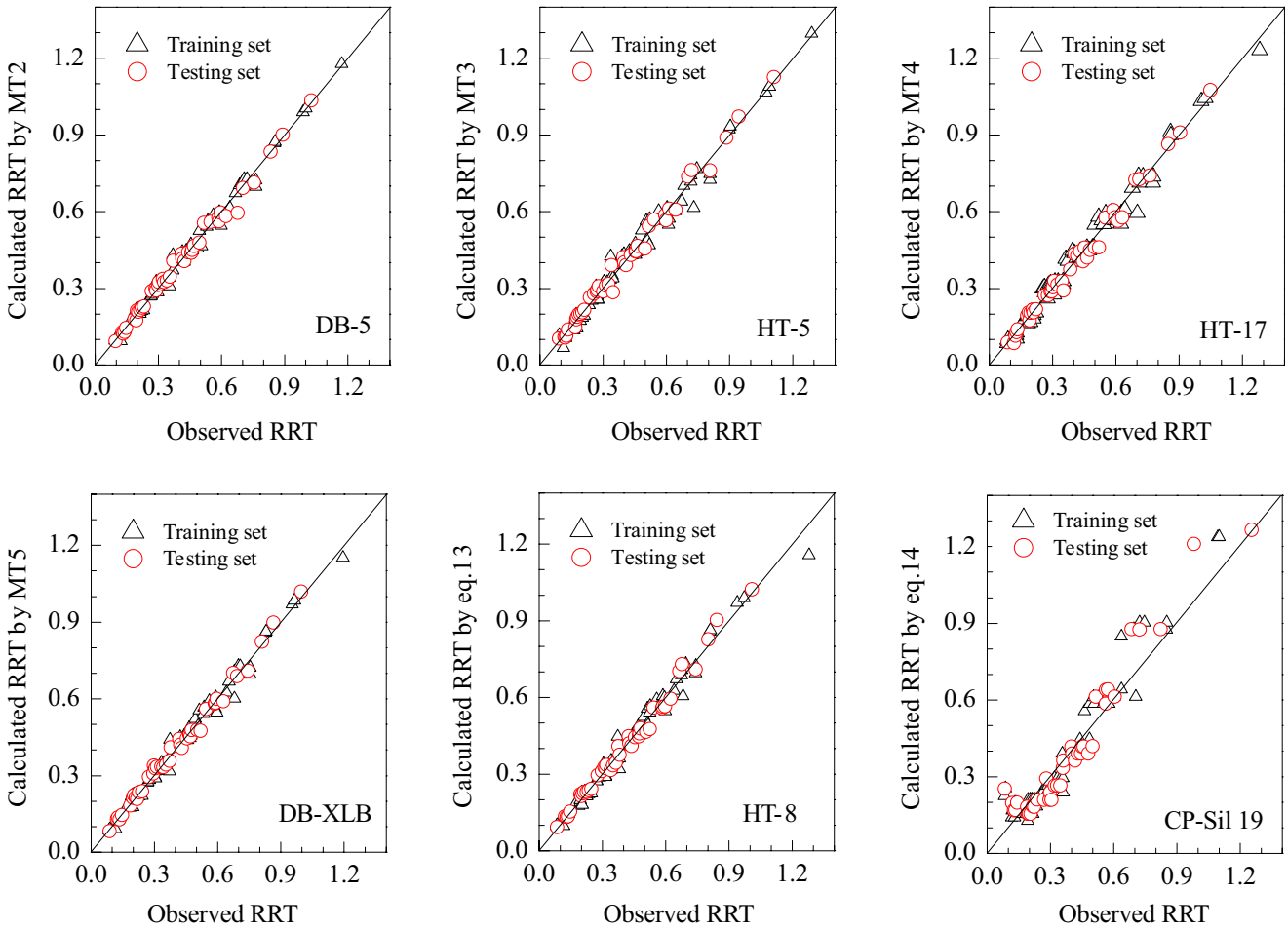

Fig. 4 Plot of RRTs calculated respectively by model MT2, MT3, MT4, MT5,MT6, and MT7 vs. observed

Comparing the model M1~M7 with MT1~MT7, it is found that there are no significant differences between the model qualities of M1~M7 derived from the whole data set including 126 PBDEs and those of MT1~MT7 from the training set consisting of 84 PBDEs. At the same time, the optimal descriptors obtained from the training sets are also the same as the ones from the whole set including 126 PBDEs. So, it is anticipated that the model M1~M7 can accurately predict the RRT values (listed in Table 4) of the 83 external PBDEs which belong to 209 PBDE congeners but their RRTs are unknown. Furthermore, in order to further strengthen the diversity of samples in the model and to improve the predictive ability of the model for the external samples, it is necessary to use the model containing 126 PBDEs so as to more effectively predict the RRT values of 209 PBDEs.

Comparison between the other RRT prediction models

There were many methods to predict the RRT values of halogenated aromatic compounds. Makino [23] reported a

Table 5 Some statistical parameters for different models

Column	*n*	Literature [17]			This paper			
		r^2	q^2	*F*	r^2	*RMSE*	q^2	*RMSV*	*F*
DB-1	100	0.990	0.988	2342.36	0.993	0.019	0.991	0.022	2135.6
DB-5	100	0.990	0.989	2348.78	0.992	0.019	0.991	0.021	1978.2
HT-5	100	0.985	0.983	1525.72	0.990	0.024	0.989	0.026	1604.9
DB-17	100	0.986	0.985	1708.92	0.990	0.024	0.989	0.025	1465.0
DB-XLB	100	0.992	0.991	2819.26	0.991	0.020	0.991	0.021	1770.4
HT-8	100	0.991	0.990	2669.07	0.987	0.025	0.987	0.025	1147.18
CP-Sil 19	100	0.967	0.959	700.51	0.937	0.093	0.930	0.098	351.17

novel classification to predict GC-RRT values and n-octanol/water partition coefficients of polychlorinated biphenyls (PCBs). Tuppurainen developed a QSAR approach to calculate the aromatic hydrocarbon receptor binding affinity of PCBs, dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) using electronic eigenvalue (EEVA) [24]. Rayne proposed a multiple-class high-resolution GC-RRT model for halogenated environmental contaminants by means of MOPAC program [25]. Recently, Wang built QSRR models for the prediction of the RRT values of PBDEs by CODESSA [17]. Some statistical parameters of the models on different stationary phases are listed in Table 5. For the convenience of comparison, 100 PBDEs are picked up from the whole set including 126 PBDES to develop QSRR models on seven stationary phases using VSMP program. The results show that there are no significant difference among the whole models Mi (i=1 to 7), training set models MTi (i=1 to 7), and the new models derived from 100 PBDEs, which further testify the reliability of the models of M1~M7. The statistical parameters of the new models are also listed in Table 5. From Table 5, for the former 4 models, this paper is better than the literature [17]. Except for the model on the CP-Sil 19 column, the models developed in this paper have not only very good estimation abilities but also very good predictive potentials.

Conclusions

The GC-RRT values of PBDEs on six stationary phases, DB-1, DB-5, DB-17, DB-XLB, HT-5, and HT-8 column, depend on six molecular descriptors, *lnMw*, E^2_{HOMO}, E^2_{LUMO}, *o*-Br, *m*-Br, and *p*-Br, while the GC-RRTs of PBDEs on CP-Sil 19 column are only related with the number of bromine substituents, i.e., *o*-Br, *m*-Br, *p*-Br, and $Br^{1/2}$. All QSRR models but one on the CP-Sil 19 column provide a reasonably good calibrated correlation coefficient (r^2= 0.984~0.993) and the LOO cross validation correlation coefficient (q^2=0.984~0.991). Meanwhile, the test results also show the predictive potentials of the models.

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References

1. Viberg H, Fredriksson A, Eriksson P (2003) Toxicol Appl Pharmacol 192:95–106
2. Chen JW, Harner T, Yang P, Quan X, Chen S, Schramm KW, Kettrup A (2003) Chemosphere 51:577–584
3. de Wit CA (2002) Chemoshphere 46:583–624
4. McDonald TA (2002) Chemosphere 46:745–755
5. Strandberg B, Dodder NG, Basu I, Hites RA (2001) Environ Sci Technol 35:1075–1083
6. Manchester-Nessvig JB, Valters K, Sonzogni WC (2001) Environ Sci Technol 35:1072–1077
7. Palm A, Cousins LT (2002) Environ Pollut 117:195–213
8. Domingo JL (2004) J Chromatogr A 1054:321–326
9. Darnerud PO, Wong J, Bergman Å, Ilbäck NG (2005) Toxicology 210:159–167
10. Hallgren S, Darnerud PO (2002) Toxicology 177:227–243
11. Korytár P, Covaci A, Boer JD, Gelbin A, Brinkman UAT (2005) J Chromatogr A 1065:239–249
12. Rayne S, Ikonomou MG (2003) J Chromatogr A 1016:235–248
13. Liu SS, Cao CZ, Li ZL (1998) J Chem Inf Comput Sci 38:387–394
14. Liu SS, Yin CS, Cai SX, Li ZL (2001) J Chem Inf Comput Sci 41:321–329
15. Liu SS (2005) Structural characterization of organic compounds by the molecular electronegativity distance vector (MEDV). Chinese Higher Education Press, Beijing
16. Liu SS, Liu Y, Yin DQ, Wang LS (2005) Chin Chem Lett 16:1559–1662
17. Wang YW, Li A, Liu HX, Zhang QH, Ma WP, Song WL, Jiang GB (2006) J Chromatogr A 1103:314–328
18. Wang YW, Liu HX, Zhao CY, Liu HX, Cai ZW, Jiang GB (2005) Environ Sci Technol 39:4961–4966
19. Liu SS, Cui SH, Shi YY, Wang LS (2002) Internet Electron J Mol Des 1:610–619
20. Liu SS, Liu HL, Yin CS, Wang LS (2003) J Chem Inf Comput Sci 43:964–969
21. Liu SS, Yin DQ, Cui SH, Wang LS (2005) Chin J Chem 23:622–626
22. Liu SS, Liu Y, Yin DQ, Wang XD, Wang LS (2006) J Sep Sci 29:296–301
23. Makino M (1999) Chemosphere 9:893–903
24. Tuppurainen K, Ruuskanen J (2000) Chemosphere 41:843–848
25. Rayne S, Ikonomou MG (2003) Anal Chem 75:1049–1057