Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1016 (2003) 235–248
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Predicting gas chromatographic retention times for the 209 polybrominated diphenyl ether congeners

Sierra Rayne [a,*], Michael G. Ikonomou [b]

[a] *Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6 Canada*
[b] *Marine Environment and Habitat Science Division, Pacific Region, Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, BC, V8L 4B2 Canada*

Received 12 June 2003; received in revised form 24 July 2003; accepted 31 July 2003

Abstract

A gas chromatographic relative retention time (GC-RRT) model was developed to predict retention times of the 209 individual polybrominated diphenyl ether (PBDE) congeners. Using the available 46 PBDE standards with mono- to deca-bromination, a multiple linear regression equation of the form RRT $= b_0 + b_1$(no. *o*-Br) $+ b_2$(no. *m*-Br) $+ b_3$(no. *p*-Br) $+ b_4(\mu) + b_5$(ln MW) was used to predict the RRTs of the remaining 163 PBDE congeners. Molecular descriptors in the model included the number of *ortho*-, *meta*-, and *para*-bromine substituents (no. *o*-Br, *m*-Br and *p*-Br, respectively), the semi-empirically calculated dipole moment (μ), and the natural logarithm of molecular weight (MW). A high level of predictability ($R^2 = 0.9972$) was obtained for the model.

Keywords: Retention prediction; Environmental analysis; Congener identification; Flame retardants; Molecular descriptors; Polybrominated diphenyl ethers

1. Introduction

Polybrominated diphenyl ether (PBDE) flame retardants (Fig. 1) are the first class of halogenated diaryl compounds to cause widespread environmental concern since polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and dichlorodiphenyltrichloroethane (DDT) were discovered in environmental samples during the 1940s to 1960s. Although other halogenated diaryl compounds have been observed in the environment over the last half-century (e.g. polychlorinated diphenyl ethers (PCDEs), polychlorinated naphthalenes (PCNs), polybrominated biphenyls (PBBs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), mixed halogenated dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs) where X = Cl, Br), the concentrations and/or toxicological importance of these compounds are generally much less than PCBs and PCDD/Fs. Only PBDEs have recently been found at high concentrations (up to the mg/kg level in sediments and higher trophic level organisms such as marine mammals) that in some cases approach or even exceed that of PCBs and DDT [1–5]. While the acute toxicity of PBDEs is thought to be low relative to PCDD/Fs and non-*ortho*-substituted PCBs [2], the

* Corresponding author. Tel.: +1-250-721-8838; fax: +1-250-721-7147.
E-mail address: srayne@uvic.ca (S. Rayne).

0021-9673/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2003.07.002

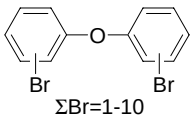

Fig. 1. Structure of polybrominated diphenyl ethers.

chronic effects may result in endocrine disruption and immunosuppression, among others [2,6,7]. However, there is limited toxicological data for only the most prevalent individual PBDE congeners in environmental samples (e.g. 2,2′,4,4′-BDE47; 2,2′,4,4′,5-BDE99; and 2,2′,4,4′,6-BDE100) [2,6], and our experience with the widely differing acute toxicities of individual PCB and PCDD/F congeners (toxic equivalent factors (TEFs) range of >6 orders of magnitude) demonstrates the necessity of identifying and monitoring concentrations of all PBDE congeners in environmental matrices. Additionally, analytical standards are available for only 46 of the 209 individual PBDE congeners, further hindering comprehensive assessments of environmental concentrations and patterns, as well as more complete toxicological investigations.

Thus, there is a need for predictive tools to help identify the remaining 163 PBDE congeners for which analytical standards are currently unavailable, but yet for which environmental data is needed. We have previously published a gas chromatographic relative retention time (GC-RRT) model for a reduced set of mono- to hexa-BDEs [8,9], but did not calculate the predicted RRTs for unknown congeners nor consider PBDEs with greater than seven bromine substituents. Here we report a GC-RRT model for all the 209 PBDE congeners from mono- to deca-brominated using a "practical" multi-linear temperature program currently used to identify known PBDE congeners in environmental samples within our high-throughput research laboratory.

2. Methods

PBDE standards obtained from Cambridge Isotope Laboratories (Andover, MA, USA) and Wellington Laboratories (Guelph, Ont., Canada) were analyzed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using a VG-Autospec mass spectrometer (Micromass, Manchester, UK) equipped with a Hewlett-Packard model 5890 series II gas chromatograph. BDE101 was generated photochemically from BDE153 in 100% CH_3CN at 302 nm irradiation and was identified as the only remaining unidentified penta-BDE congener from the primary photodebromination of BDE153 (analytical standards were available for the other two primary photodebromination products, BDEs 99 and 118, although BDE118 was initially identified in the photoproduct mixture using previously published RRT models for a smaller set of mono- to hexa-BDEs [8,9]). Details on this debromination process, as well as the general solution photochemistry of BDE153, are soon to be published. The GC was operated in the splitless injection mode, and the splitless injector purge valve was activated 2 min after sample injection. The volume injected was 1 μl of sample plus 0.5 μl of air. A 15 m DB-5HT column (0.25 mm i.d. × 0.1 μm film thickness) coupled with 1.2 m of pre-column of the same properties was used with UHP-He at 42 kPa and the following temperature program: hold at 100 °C for 1 min; 2 °C/min to 140 °C; 4 °C/min to 220 °C; 8 °C/min to 330 °C; and hold 1.2 min. The splitless injector port, direct HRGC/HRMS interface, and the HRMS ion source were maintained at 300, 275, and 315 °C, respectively. Further details on the HRGC/HRMS methods for individual PBDE congener identification and quantitation are published elsewhere [3,4,8–11].

Physicochemical properties for the analytes of interest were calculated using CambridgeSoft Chem3D Ultra 6.0 (Cambridge, USA). Molecular structures were optimized using the MM2 energy minimization program. The physicochemical properties were then calculated using the MOPAC2000 MNDO-PM3 program; a table of these values for the 209 PBDE congeners is not included in the manuscript but is available from the corresponding author. Data were subsequently treated using Microsoft Excel 2002 (Redmond, WA, USA), and multiple linear regression models were developed using forward selection, backward elimination, and stepwise selection methods with KyPlot v.2.0 b.13 (Tokyo, JPN) and SPSS for Windows v.10.0.5 (Chicago, USA). Potential variables examined in the RRT model included dipole moment, ionization potential, number of *ortho*-, *meta*-, and *para*-bromine substituents, number of total bromine substituents, square of the number of total bromine

Table 1
Observed and predicted RRTs for the 46 mono- to deca-brominated diphenyl ethers used in constructing the model

PBDE congener	Observed RRT	Predicted RRT[a]	ΔRRT[b]
2-BDE1	0.256	0.234 ± 0.008	0.022 (49.3)
3-BDE2	0.270	0.265 ± 0.008	0.005 (11.8)
4-BDE3	0.284	0.283 ± 0.009	0.001 (1.8)
2,6-BDE10	0.464	0.496 ± 0.008	−0.032 (−71.9)
2,4-BDE7	0.530	0.560 ± 0.006	−0.030 (−66.6)
2,4′-BDE8	0.561	0.556 ± 0.005	0.005 (11.7)
3,3′-BDE11	0.561	0.559 ± 0.009	0.002 (4.3)
3,4-BDE12	0.578	0.588 ± 0.005	−0.010 (−22.1)
3,4′-BDE13	0.584	0.583 ± 0.005	0.001 (3.2)
4,4′-BDE15	0.604	0.593 ± 0.007	0.011 (24.6)
2,4,6-BDE30	0.701	0.739 ± 0.006	−0.038 (−85.3)
2,4′,6-BDE32	0.755	0.752 ± 0.006	0.003 (7.3)
2,2′,4-BDE17	0.773	0.751 ± 0.006	0.022 (48.7)
2,3′,4-BDE25	0.778	0.776 ± 0.004	0.002 (4.4)
2′,3,4-BDE33	0.796	0.785 ± 0.005	0.011 (25.1)
2,4,4′-BDE28	0.796	0.793 ± 0.005	0.003 (7.1)
3,3′,4-BDE35	0.813	0.811 ± 0.006	0.002 (4.2)
3,4,4′-BDE37	0.829	0.825 ± 0.006	0.004 (9.0)
2,4,4′,6-BDE75	0.914	0.937 ± 0.005	−0.023 (−50.6)
2,2′,4,5′-BDE49	0.928	0.919 ± 0.006	0.009 (19.6)
2,3′,4′,6-BDE71	0.930	0.939 ± 0.010	−0.009 (−21.2)
2,2′,4,4′-BDE47	0.950	0.941 ± 0.005	0.009 (19.7)
2,3′,4,4′-BDE66	0.969	0.972 ± 0.004	−0.003 (−7.4)
3,3′,4,4′-BDE77	1.000	0.999 ± 0.007	0.001 (1.2)
2,2′,4,4′,6-BDE100	1.054	1.056 ± 0.006	−0.002 (−4.8)
2,2′,4,5,5′-BDE101	1.062	1.062 ± 0.007	0.000 (0.5)
2,3′,4,4′,6-BDE119	1.064	1.091 ± 0.004	−0.027 (−60.9)
2,2′,4,4′,5-BDE99	1.084	1.082 ± 0.004	0.002 (4.1)
2,3,4,5,6-BDE116	1.089	1.066 ± 0.006	0.023 (51.8)
2,3′,4,4′,5-BDE118	1.107	1.119 ± 0.005	−0.012 (−26.5)
2,2′,3,4,4′-BDE85	1.130	1.091 ± 0.004	0.039 (88.3)
3,3′,4,4′,5-BDE126	1.139	1.132 ± 0.008	−0.012 (−26.8)
2,3,3′,4,4′-BDE105	1.145	1.151 ± 0.005	0.020 (45.3)
2,2′,4,4′,6,6′-BDE155	1.137	1.125 ± 0.008	0.005 (10.5)
2,2′,4,4′,5,6′-BDE154	1.155	1.166 ± 0.005	−0.011 (−24.9)
2,2′,4,4′,5,5′-BDE153	1.184	1.198 ± 0.004	−0.014 (−31.9)
2,2′,3,4,4′,6′-BDE140	1.200	1.170 ± 0.005	0.030 (67.2)
2,2′,3,4,4′,5-BDE138	1.218	1.202 ± 0.004	0.011 (24.8)
2,3,4,4′,5,6-BDE166	1.218	1.207 ± 0.004	0.016 (35.4)
2,2′,3,4,4′,5′,6-BDE183	1.255	1.275 ± 0.004	−0.020 (−44.4)
2,2′,3,4,4′,5,6-BDE181	1.288	1.278 ± 0.004	0.010 (22.7)
2,3,3′,4,4′,5,6-BDE190	1.292	1.310 ± 0.005	−0.018 (−41.3)
2,2′,3,3′,4,5,5′,6,6′-BDE208	1.394	1.381 ± 0.009	0.013 (29.9)
2,2′,3,3′,4,4′,5,6,6′-BDE207	1.400	1.401 ± 0.008	−0.001 (−1.2)
2,2′,3,3′,4,4′,5,5′,6-BDE206	1.412	1.440 ± 0.008	−0.028 (−62.2)
2,2′,3,3′,4,4′,5,5′,6,6′-BDE209	1.472	1.465 ± 0.010	0.007 (16.5)

[a] RRTs were calculated as relative to 3,3′,4,4′-BDE7 and include standard errors for the predicted values.
[b] ΔRRT was calculated as observed minus predicted RRT; values in parentheses are deviations from observed RTs in seconds.

substituents, and the molecular weight and various mathematical transformations of these variables (e.g. inverse, logarithmic, exponential, square/square root, and the trigonometric functions [sin, cos, tan]). RRTs were obtained by dividing the RT for the analyte of interest by the RT of 3,3′,4,4′-BDE77, which had a RT of 37.24 min using the instrument conditions described above. Other combinations of retention time normalization were examined, including other individual congeners from mono- to deca-brominated, as well as combinations of low and high MW congeners (e.g. BDEs 28 and 153). These other normalization techniques did not improve the quality of the model.

3. Results and discussion

A gas chromatographic retention time model for the 209 polybrominated diphenyl ether congeners was developed. The multiple linear regression equation shown below utilizes the bromine substitution pattern, semi-empirical MNDO-PM3 method calculated dipole moment, and molecular weight of individual

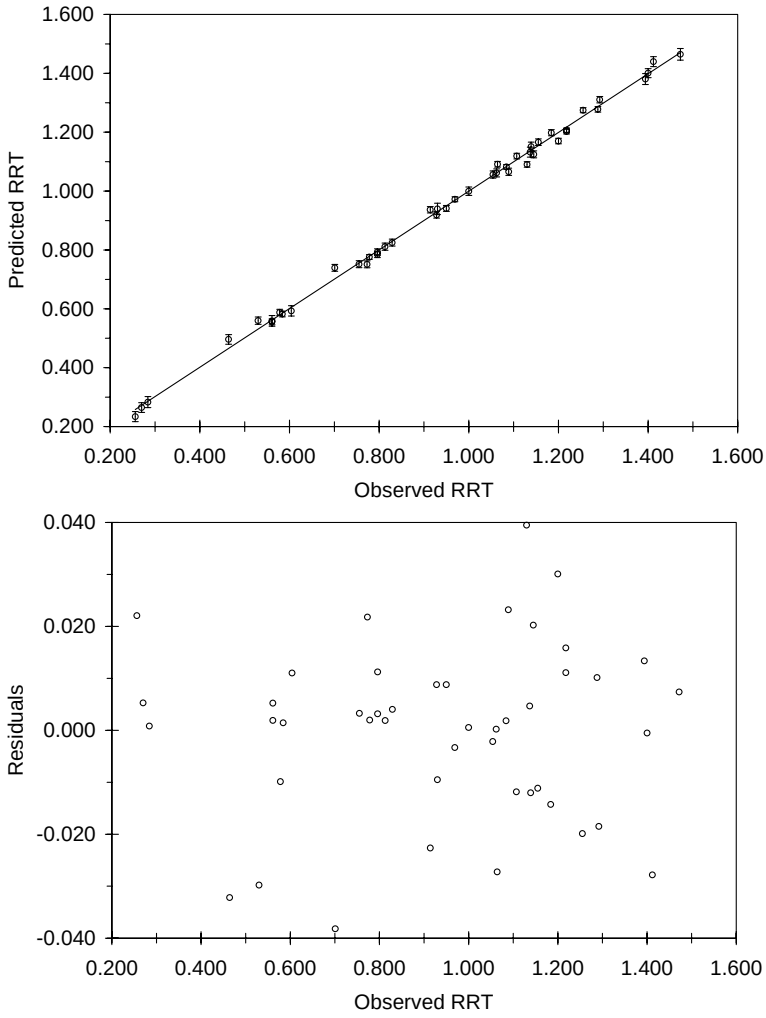

Fig. 2. RRT model for PBDEs (error bars are 95% confidence intervals on predicted RRT values) and distribution of residuals over the range of observed RRTs. A regression equation of the form predicted RRT = 0.9972(observed RRT) + 0.0026 with an $R^2 = 0.9972$ is shown.

Table 2
Predicted RRTs for the 163 di- to nona-brominated diphenyl ethers for which analytical standards were not currently available at the time of model construction

PBDE congener	Predicted RRT[a]	PBDE congener	Predicted RRT	PBDE congener	Predicted RRT	PBDE congener	Predicted RRT
2,2′-BDE4	0.501 ± 0.033	2,3,3′,5-BDE57	0.943 ± 0.027	2,3,3′,5,5′-BDE111	1.084 ± 0.031	2,2′,3,3′,4,6,6′-BDE176	1.214 ± 0.031
2,5-BDE9	0.524 ± 0.031	2,3,3′,5′-BDE58	0.948 ± 0.027	2,3,4,4′,6-BDE115	1.087 ± 0.020	2,3′,4,4′,5′,6-BDE168	1.214 ± 0.023
2,3′-BDE6	0.532 ± 0.031	2,3,4′,5-BDE63	0.956 ± 0.020	2,3′,4′,5′,6-BDE125	1.087 ± 0.022	2,3,3′,4,4′,6-BDE158	1.217 ± 0.023
2,3-BDE5	0.535 ± 0.031	2,3′,4,5′-BDE68	0.959 ± 0.020	2,2′,3,3′,6,6′-BDE136	1.097 ± 0.032	2,2′,3,3′,4,4′-BDE128	1.218 ± 0.023
3,5-BDE14	0.563 ± 0.033	2,3,3′,4-BDE55	0.962 ± 0.020	2,3′,4,5,5′-BDE120	1.100 ± 0.024	2,3,3′,4,5,5′-BDE159	1.222 ± 0.030
2,2′,6-BDE19	0.701 ± 0.030	2,3′,4,5-BDE67	0.964 ± 0.020	2,3,3′,4′,5-BDE107	1.104 ± 0.023	2,2′,3,4,5,6,6′-BDE186	1.224 ± 0.031
2,3,6-BDE24	0.723 ± 0.026	2,3′,4′,5-BDE70	0.964 ± 0.020	2,3′,4′,5,5′-BDE124	1.108 ± 0.023	2,3,3′,4′,5,5′-BDE162	1.227 ± 0.029
2,2′,5-BDE18	0.724 ± 0.026	2,3,3′,4′-BDE56	0.965 ± 0.020	2,2′,3,5,6,6′-BDE152	1.108 ± 0.032	2,2,3,4,4′,6,6′-BDE184	1.230 ± 0.031
2,2′,3-BDE16	0.738 ± 0.027	2,3,4,5-BDE61	0.967 ± 0.020	2,3,3′,4,5-BDE106	1.108 ± 0.023	2,2′,3,3′,5,5′,6-BDE178	1.235 ± 0.036
2,3′,6-BDE27	0.739 ± 0.027	3,3′,5,5′-BDE80	0.968 ± 0.033	2,3,3′,4,5′-BDE108	1.109 ± 0.023	2,3′,4,4′,5,5′-BDE167	1.242 ± 0.026
2,3′,5-BDE26	0.762 ± 0.027	2,3′,4′,5′-BDE76	0.972 ± 0.021	2,3,3′,4′,5′-BDE122	1.116 ± 0.024	2,3,3′,4,4′,5-BDE156	1.242 ± 0.026
2,3,5-BDE23	0.766 ± 0.027	2,4,4′,5-BDE74	0.973 ± 0.020	2,3,4,4′,5-BDE114	1.120 ± 0.021	2,2′,3,4,5,5′,6-BDE185	1.246 ± 0.030
2,3′,5′-BDE34	0.766 ± 0.027	2,2′,3,6,6′-BDE96	0.980 ± 0.030	2,2′,3,4′,6,6′-BDE150	1.121 ± 0.028	2,2′,3,3′,4,5′,6′-BDE177	1.247 ± 0.030
2,3,3′-BDE20	0.767 ± 0.027	2,3,4,4′-BDE60	0.981 ± 0.019	2,3′,4,4′,5′-BDE123	1.125 ± 0.021	2,3,3′,4,4′,5′-BDE157	1.248 ± 0.026
2,4′,5-BDE31	0.775 ± 0.021	3,3′,4,5′-BDE79	0.992 ± 0.025	2,2′,3,4,6,6′-BDE145	1.126 ± 0.028	2,2′,3,3′,4,5,6′-BDE174	1.252 ± 0.030
2,4,5-BDE29	0.782 ± 0.021	3,3′,4,5-BDE78	0.997 ± 0.025	2,2′,3,3′,5,6′-BDE135	1.134 ± 0.031	2,2′,3,3′,4,5′,6-BDE175	1.253 ± 0.030
2,3,4′-BDE22	0.784 ± 0.021	2,2′,4,6,6′-BDE104	1.005 ± 0.027	3,3′,4,5,5′-BDE127	1.134 ± 0.030	2,2′,3,4′,5,5′,6-BDE187	1.253 ± 0.030
2,3,4-BDE21	0.788 ± 0.022	3,4,4′,5-BDE81	1.008 ± 0.023	2,2′,3,5,5′,6-BDE151	1.135 ± 0.031	2,2′,3,3′,4,5,6-BDE173	1.261 ± 0.030
3,3′,5-BDE36	0.793 ± 0.030	2,2′,3,5,6′-BDE94	1.018 ± 0.027	2,2′,3,3′,5,6-BDE134	1.148 ± 0.031	2,2′,3,4,4′,5,6′-BDE182	1.265 ± 0.028
3,4′,5-BDE39	0.800 ± 0.025	2,2′,3,5′,6-BDE95	1.020 ± 0.027	2,2′,3,4′,5,6′-BDE148	1.150 ± 0.025	3,3′,4,4′,5,5′-BDE169	1.273 ± 0.032
3,4,5-BDE38	0.818 ± 0.024	2,2′,3,5,6-BDE93	1.023 ± 0.027	2,2′,3,4,5′,6-BDE144	1.150 ± 0.025	2,2′,3,3′,4,4′,6-BDE171	1.281 ± 0.028
2,2′,6,6′-BDE54	0.839 ± 0.030	2,2′,4,5′,6-BDE103	1.030 ± 0.022	2,2′,3,3′,4,6′-BDE132	1.154 ± 0.025	2,2′,3,3′,4,5,5′-BDE172	1.284 ± 0.032
2,2′,5,6′-BDE53	0.872 ± 0.026	2,2′,3,3′,6-BDE84	1.031 ± 0.028	2,2′,3,4′,5,6-BDE147	1.163 ± 0.025	2,3,3′,4,5,5′,6-BDE192	1.285 ± 0.032
2,2′,3,6′-BDE46	0.872 ± 0.026	2,2′,3,4′,6′-BDE98	1.037 ± 0.022	2,2′,3,4,5,6′-BDE143	1.163 ± 0.025	2,3,3′,4′,5,5′,6-BDE193	1.291 ± 0.032
2,2′,3,6-BDE45	0.878 ± 0.026	2,2′,3,4,6′-BDE89	1.041 ± 0.022	2,2′,3,4′,5′,6-BDE149	1.163 ± 0.025	2,2′,3,4,4′,5,5′-BDE180	1.300 ± 0.029
2,2′,4,6′-BDE51	0.891 ± 0.023	2,2′,4,5,6′-BDE102	1.042 ± 0.022	2,2′,3,4,5,6-BDE142	1.164 ± 0.025	2,2′,3,3′,4,4′,5-BDE170	1.309 ± 0.028
2,2′,5,5′-BDE52	0.895 ± 0.025	2,2′,3,4,6-BDE88	1.042 ± 0.022	2,2′,3,3′,4,6-BDE131	1.167 ± 0.025	2,3,3′,4,4′,5′,6-BDE191	1.309 ± 0.028
2,2′,4,6-BDE50	0.896 ± 0.023	2,2′,3,4′,6-BDE91	1.045 ± 0.023	2,2′,3,3′,5,5′-BDE133	1.168 ± 0.033	2,2′,3,3′,4,4′,6,6′-BDE197	1.324 ± 0.035
2,3,5,6-BDE65	0.905 ± 0.025	2,3,3′,5′,6-BDE113	1.049 ± 0.028	2,3,3′,5,5′,6-BDE165	1.171 ± 0.033	2,3,3′,4,4′,5,5′-BDE189	1.337 ± 0.032
2,2′,3,5-BDE43	0.913 ± 0.025	2,2′,3,5,5′-BDE92	1.055 ± 0.028	2,2′,3,4,4′,6-BDE139	1.181 ± 0.025	2,2′,3,3′,4,5,5′,6′-BDE199	1.343 ± 0.036
2,3,3′,6-BDE59	0.917 ± 0.025	2,3,3′,5,6-BDE112	1.059 ± 0.028	2,3,3′,4,5′,6-BDE161	1.190 ± 0.025	2,2′,3,3′,4,5,6,6′-BDE200	1.343 ± 0.036
2,2′,3,5′-BDE44	0.917 ± 0.025	2,2′,3,3′,5-BDE83	1.060 ± 0.028	2,2′,3,4,5,5′-BDE141	1.191 ± 0.025	2,2′,3,3′,4,5′,6,6′-BDE201	1.343 ± 0.036
2,3′,5′,6-BDE73	0.918 ± 0.025	2,3′,4,5′,6-BDE121	1.069 ± 0.021	2,2′,3,4′,5,5′-BDE146	1.191 ± 0.025	2,2′,3,3′,5,5′,6,6′-BDE202	1.343 ± 0.036
2,2′,3,3′-BDE40	0.923 ± 0.026	2,3,4′,5,6-BDE117	1.070 ± 0.021	2,2′,3,3′,4,5′-BDE130	1.194 ± 0.025	2,2′,3,4,4′,5,5′,6-BDE203	1.343 ± 0.036
2,3′,4,6-BDE69	0.927 ± 0.019	2,2′,3,4′,5-BDE90	1.071 ± 0.021	2,2′,3,3′,5,6,6′-BDE179	1.195 ± 0.036	2,2′,3,4,4′,5,6,6′-BDE204	1.343 ± 0.036
2,3,4,6-BDE62	0.929 ± 0.019	2,3,3′,4,6-BDE109	1.077 ± 0.021	2,3,3′,4,5,6-BDE160	1.196 ± 0.026	2,3,3′,4,4′,5,5′,6-BDE205	1.343 ± 0.036
2,3,4′,6-BDE64	0.929 ± 0.019	2,2′,3,4′,5′-BDE97	1.080 ± 0.021	2,2′,3,3′,4,5-BDE129	1.199 ± 0.026	2,2′,3,3′,4,5,5′,6-BDE198	1.347 ± 0.036
2,2′,4,5-BDE48	0.932 ± 0.019	2,2′,3,4,5′-BDE87	1.080 ± 0.021	2,3,3′,4′,5,6-BDE163	1.199 ± 0.026	2,2′,3,3′,4,4′,5,6′-BDE196	1.359 ± 0.034
2,2′,3,4′-BDE42	0.936 ± 0.020	2,2′,3,4,5-BDE86	1.082 ± 0.021	2,3,3′,4′,5′,6-BDE164	1.202 ± 0.026	2,2′,3,3′,4,4′,5,6-BDE195	1.374 ± 0.033
2,2′,3,4-BDE41	0.939 ± 0.020	2,3,3′,4′,6-BDE110	1.083 ± 0.021	2,2′,3,4,4′,5-BDE137	1.210 ± 0.023	2,2′,3,3′,4,4′,5,5′-BDE194	1.399 ± 0.035
2,3′,5,5′-BDE72	0.940 ± 0.027	2,2′,3,3′,4-BDE82	1.083 ± 0.021	2,2′,3,4′,5,6,6′-BDE188	1.213 ± 0.031		

[a] RRTs were calculated as relative to 3,3′,4,4′-BDE7 and include standard errors for the predicted values.

congeners to successfully predict the relative retention times of 46 PBDE congeners for which analytical standards were available,

$$\mathrm{RRT} = b_0 + b_1(\text{no. } o\text{-Br}) + b_2(\text{no. } m\text{-Br}) + b_3(\text{no. } p\text{-Br}) + b_4(\mu) + b_5(\ln \mathrm{MW})$$

where RRT is the retention time for the congener of interest relative to that of 3,3′,4,4′-BDE77, b_0 to b_5 are the regression coefficients, no. *o*-Br is the number of ortho bromine substituents, no. *m*-Br is the number of meta bromine substituents, no. *p*-Br is the number of para bromine substituents, μ is the dipole moment in Debye, and ln MW is the natural logarithm of the molecular weight (Table 1 and Fig. 2). This model was then used to predict the RRTs for the remaining 163 PBDE congeners for which analytical standards were not available (Table 2).

The regression model was generated using the backward elimination method (criterion: probability for *F*-to-remove ≥0.100) and had a multiple correlation coefficient (R) of 0.9986 and a coefficient of multiple determination (R^2) of 0.9972 (Table 3), indicating that >99.7% of the total variation in the predicted RRT values is explained by the fitted model. Forward selection and stepwise selection provided similar results with equally strong models using the same variables in the optimized model. The *F*-value for the model, a statistical measure of goodness of fit, was 2843, which greatly exceeds the critical *F*-value 2.5 at $\alpha = 0.05$, with a $P(F > F_{\mathrm{crit}}) = 6.7 \times 10^{-50}$. These results suggest that the regression explained by the model is significant. The residuals between predicted and observed RRTs show little systematic tendency when plotted against observed RRT (Fig. 2). The standard error (S.E.) for the model was 0.01774, corresponding to a coefficient of variation (CV) of 0.01892 and %CV = 1.89, which is the relative percentage of error at the mean of the RRT values. To further examine the model's validity and accuracy, the PRESS statistic was investigated. The PRESS statistic arises from generating a regression equation using $(N - 1)$ observations, predicting the RRT value for the omitted observation, and summing the squared residuals for each of the N models created in this manner. For the current model, the PRESS statistic was 0.01645 which is a 1.76% error at the mean, implying a very strong model.

Table 3
Regression coefficients and statistical descriptors for the RRT model: $\mathrm{RRT} = b_0 + b_1(\text{no. } o\text{-Br}) + b_2(\text{no. } m\text{-Br}) + b_3(\text{no. } p\text{-Br}) + b_4(\mu) + b_5(\ln \mathrm{MW})$

	Value ± S.E.[a] (R.S.E.[b])
b_0	−6.5967 ± 0.2526 (3.8%)
b_1	−0.0763 ± 0.0071 (9.3%)
b_2	−0.0410 ± 0.0068 (16.5%)
b_3	−0.0210 ± 0.0108 (51.7%)
b_4	0.0120 ± 0.0061 (50.9%)
b_5	1.2474 ± 0.0462 (3.7%)
R	0.9986
$F_{\mathrm{obs}}/F_{\mathrm{crit}}$[c]	2843/2.5
$P(F_{\mathrm{obs}} > F_{\mathrm{crit}})$[d]	6.7×10^{-50}
S.E.[e]	0.01774
CV[f]	0.01892
PRESS[g] statistic	0.01645
N[h]	46

[a] Standard error of the regression coefficients.
[b] Relative standard error of the regression coefficients.
[c] Observed and critical *F*-values.
[d] Probability that F_{obs} is greater than the critical *F*-value (F_{crit}) at $\alpha = 0.05$.
[e] Standard error of the regression model.
[f] Coefficient of variation.
[g] PRESS, predicted error sum of squares.
[h] Number of observations.

Additional testing of the model was performed by dividing the training set (the 46 congeners for which analytical standards were available) into two subsets of 23 congeners each (i.e. assigning the first eluting congener to subset 1 (the "odd" set), the second eluting congener to subset 2 (the "even" set), etc.). Multiple linear regression was performed using the five independent variables discussed above on each subset to generate a corresponding RRT model. Each model was then used to predict the RRTs for the remaining 23 congeners in the other subset for which RRTs were known. Good predictive ability was demonstrated by this approach, as is shown in Fig. 3 for the "odd" ($R^2 = 0.9953$; predicted RRT = 0.9873(observed RRT) + 0.0070) and "even" ($R^2 = 0.9983$; predicted RRT = 0.9994(observed RRT)+0.0027) sets. RRTs were also calculated using a 1/2-RRT model approach initially applied to polychlorinated diphenyl ethers [12] and the results of this model are shown in Fig. 4. The 1/2-RRT model, based only on bromine substitution pattern, has a weaker fit ($R^2 = 0.9856$; predicted RRT = 0.9776(observed RRT) + 0.0092) than the

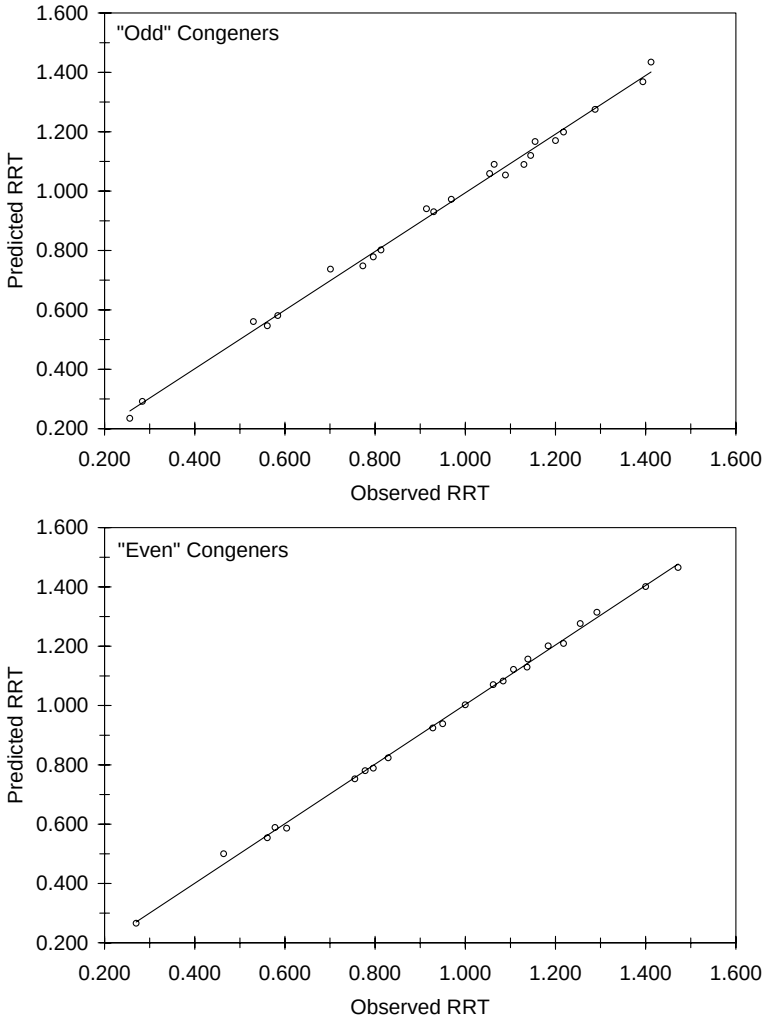

Fig. 3. RRT models for PBDEs over the range of observed RRTs using training set of every second "odd" (e.g. BDEs $1, 3, \ldots$) and "even" (e.g. BDEs $2, 10, \ldots$) congener from the ordered list of congener elution times given in Table 1. Regression equations of the form predicted RRT $= 0.9873$(observed RRT) $+ 0.0070$ with an $R^2 = 0.9953$ and predicted RRT $= 0.9994$(observed RRT) $+ 0.0027$ with an $R^2 = 0.9983$ are shown, respectively.

models presented in Fig. 2 ($R^2 = 0.9972$) and Fig. 3 ($R^2 = 0.9953$ and 0.9983), and appears to have difficulty addressing bromine substitution skewed to one aromatic ring as is evident in the outlying predicted RRTs for 2,3,4,5,6-BDE116 and 2,3,4,4′,5,6-BDE166. As well, the slope of the 1/2-RRT model is lower than the ideal value of unity more closely approached using the other models ($m = 0.9972$, 0.9873, and 0.9994 for Figs. 2 and 3, respectively). The results of these three tests, along with that of the PRESS statistic, suggest a superior predictive model using the approach shown in Fig. 2 and Table 3. Furthermore, the R^2 value for the model in Fig. 2 (0.9972) is in good agreement with isothermal GC-RRT models developed for PCDEs (0.996−0.998) [12], polyaromatic hydrocarbons (0.990 [13], 0.987 [14], and 0.993 [15]), PCDD/Fs (0.9995 [16] and 0.927−0.981 [14]), and PCBs (0.997 [17], 0.9973 [18], and 0.964 [14]).

The emphasis of the current model is estimating RRTs for the 163 PBDE congeners without available

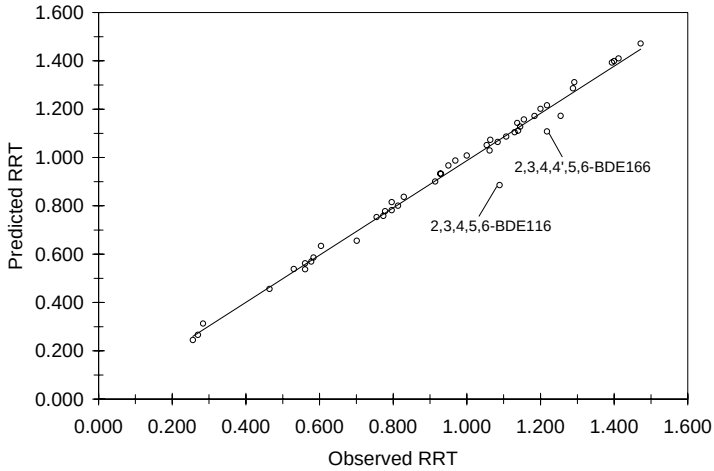

Fig. 4. RRT model for PBDEs over the range of observed RRTs using the 1/2-RRT model previously published for polychlorinated diphenyl ethers (PCDEs) as described in the manuscript. A regression equation of the form predicted RRT = 0.9776(observed RRT) + 0.0092 with an $R^2 = 0.9856$ is shown.

analytical standards using a realistic retention time program for a commercial or research laboratory regularly analyzing environmental or experimental samples for this class of analytes. It must be stressed that the model is not attempting to set out a theoretical framework for how PBDEs behave within a gas chromatograph, nor was the aim to optimize the predictability of the model without considering the length of the GC run. In principle, an isothermal or iso-linear temperature program would be needed to fully optimize the predictive ability of the model, as has been demonstrated elsewhere for PAHs, [13–15] PCBs, [14,17] PCDD/Fs, [14,16] and PCDEs [12], although our model optimized for analytical utility in a high-throughput laboratory using a multi-linear temperature programming approach performs either

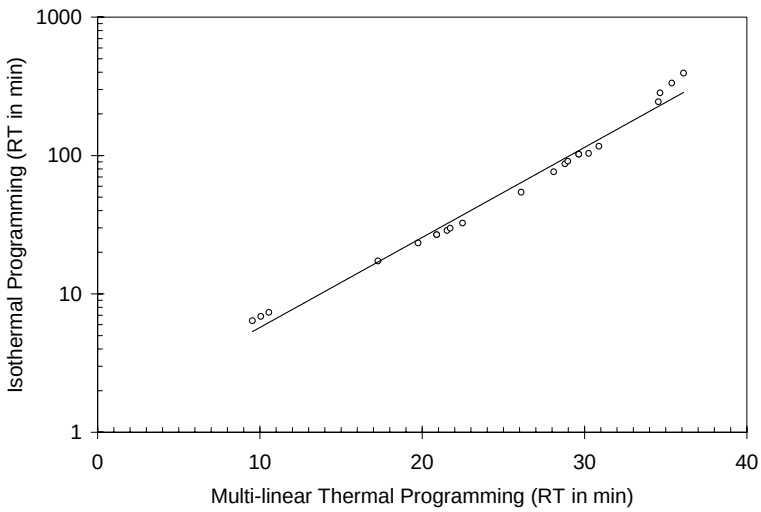

Fig. 5. Observed retention times for the mono- through tetra-brominated PBDE standards shown in Table 1 using the multi-linear and isothermal temperature programs described in the manuscript. A regression equation of the form isothermal elution time = 1.2785 × exp(0.1498 × multi-linear thermal elution time) with an $R^2 = 0.9850$ is shown.

as good or better than the isothermal/iso-linear models. Thus, while our model also has a high level of predictability, its advantage lies in the retention of predictability with the use of multi-linear temperature programming. Without the multi-linear temperature programming, the higher brominated congeners, especially those with more than five to six bromines, would take unreasonably long times to elute. While theoretically more useful in a predictive model, such long elution times (>1 h) are practically troublesome in high-throughput research and commercial labs due to challenges associated in maintaining long-term instrument stability and retention time reproducibility. Indeed, to demonstrate this problem, we analyzed the 46 PBDE standards using the instrumental conditions described above except with an isothermal GC temperature program set at 120 °C. As is seen in Fig. 5, under the isothermal conditions the first eluting congener (BDE1) comes off the column at 6.40 min; however, the last available congener for which a reliable response was observed is BDE66 at 394.77 min (i.e. ∼6 h 35 min). Extrapolating the regression equation shown in Fig. 5 out to the observed multi-linear thermal programming retention time for BDE209 (54.81 min) gives a predicted isothermal retention time of 4704 min (78 h, 24 min). Thus, an isothermal model for full congener PBDE retention times appears impractical. A strong correlation is observed between the isothermal and multi-linear programming, suggesting the validity of our multi-linear approach to predicting GC retention times in the case of analyte groupings having an extremely wide range of potential isothermal elution times.

Additionally, it is anticipated a number of the >160 as yet unknown PBDE congeners will be identified from rigorous, yet routine, analyses of multiple environmental samples given the difficulty in synthesizing many of the PBDE congeners. Unfortunately, the lability of the aryl-bromine bond compared to the stronger aryl-chlorine and aryl-fluorine bonds makes the needed coupling reactions between two brominated aryl precursors a non-trivial exercise. These various unknown congeners may arise from environmental debromination of the penta-, octa-, and deca-BDE technical mixtures in major usage today [10,11], and the resulting debromination patterns are known to depend on the environmental matrix (e.g. seawater, freshwater, sediments, and soil) and debrominating agent (e.g. photolysis, microorganisms, abiotic thermal reduction). Thus, by careful choice of the parent congener and the mode of debromination, select congeners may be “synthesized” by such non-traditional methods.

Table 4
Predicted range of potential identities for the 19 unknown PBDE congeners commonly observed in freshwater and marine sediment and biota samples

Number of Br	RRT	Potential identities
2	0.562	BDEs 6/5/14
3	0.715	BDEs 19/24/18/16/27
3	0.778	BDEs 16/23/34/20/31/29/22/21/36/39
5	1.012	BDEs 104/81/94/95/93/103/84
5	1.018	BDEs 104/81/94/95/93/103/84/98/89
5	1.021	BDEs 104/81/94/95/93/103/84/98/89/102/88
5	1.034	BDEs 94/95/93/103/84/98/89/102/88/91/113/92/112/83
5	1.041	BDEs 94/95/93/103/84/98/89/102/88/91/113/92/112/83
5	1.044	BDEs 94/95/93/103/84/98/89/102/88/91/113/92/112/83
5	1.066	BDEs 91/113/92/112/83/121/117/90/109/97/87/86/110/82/111/125/136
5	1.075	BDEs 91/113/92/112/83/121/117/90/109/97/87/86/110/82/111/115/125/136
5	1.108	BDEs 111/115/125/136/120/107/124/152
6	1.168	BDEs 134/148/144/132/147/143/149/142/131/133/165/139/161/141/146
6	1.177	BDEs 134/148/144/132/147/143/149/142/131/133/165/139/161/141/146/130/179/160/129/163/164
8	1.320	BDEs 189/199/200/201/202/203/204/205/198
8	1.323	BDEs 189/199/200/201/202/203/204/205/198
8	1.326	BDEs 189/199/200/201/202/203/204/205/198/196
8	1.335	BDEs 189/199/200/201/202/203/204/205/198/196
8	1.340	BDEs 189/199/200/201/202/203/204/205/198/196

To demonstrate the potential utility of the model, our group routinely observes a number of unknown PBDE congeners by HRGC/HRMS in environmental samples. Using the predicted RRTs and their associated standard errors shown in Table 2, we can assign potential identities to these 19 congeners as shown in Table 4. Synthetic efforts should possibly be directed at these 84 potential congener assignments

Table 5
Bromine substitution patterns, semi-empirical MNDO-PM3 method calculated dipole moments, natural logarithms of the molecular weight, and observed retention times for the 46 PBDE congeners used in constructing the RRT model

	Number of *ortho*-Br	Number of *meta*-Br	Number of *para*-Br	Dipole (Debye)	ln MW	RT (min)
2-BDE1	1	0	0	1.9774	5.5179	9.54
3-BDE2	0	1	0	1.5977	5.5179	10.06
4-BDE3	0	0	1	1.4705	5.5179	10.56
2,6-BDE10	2	0	0	1.5916	5.7930	17.27
2,4-BDE7	1	0	1	2.2789	5.7930	19.74
2,4′-BDE8	1	0	1	1.9439	5.7930	20.89
3,3′-BDE11	0	2	0	0.9434	5.7930	20.89
3,4-BDE12	0	1	1	1.6749	5.7930	21.53
3,4′-BDE13	0	1	1	1.2311	5.7930	21.73
4,4′-BDE15	0	0	2	0.4317	5.7930	22.49
2,4,6-BDE30	2	0	1	1.1825	6.0086	26.10
2,4′,6-BDE32	2	0	1	2.2259	6.0086	28.10
2,2′,4-BDE17	2	0	1	2.1834	6.0086	28.79
2,3′,4-BDE25	1	1	1	1.3061	6.0086	28.97
2′,3,4-BDE33	1	1	1	2.0351	6.0086	29.65
2,4,4′-BDE28	1	0	2	1.0399	6.0086	29.65
3,3′,4-BDE35	0	2	1	1.2869	6.0086	30.26
3,4,4′-BDE37	0	1	2	0.7735	6.0086	30.89
2,4,4′,6-BDE75	2	0	2	0.9633	6.1858	34.02
2,2′,4,5′-BDE49	2	1	1	1.1768	6.1858	34.55
2,3′,4′,6-BDE71	2	1	1	2.8659	6.1858	34.65
2,2′,4,4′-BDE47	2	0	2	1.3409	6.1858	35.38
2,3′,4,4′-BDE66	1	1	2	0.9892	6.1858	36.10
3,3′,4,4′-BDE77	0	2	2	0.3051	6.1858	37.24
2,2′,4,4′,6-BDE100	3	0	2	1.6373	6.3363	39.24
2,2′,4,5,5′-BDE101	2	2	1	0.8274	6.3363	39.56
2,3′,4,4′,6-BDE119	2	1	2	1.6152	6.3363	39.61
2,2′,4,4′,5-BDE99	2	1	2	0.8585	6.3363	40.36
2,3,4,5,6-BDE116	2	2	1	1.1623	6.3363	40.57
2,3′,4,4′,5-BDE118	1	2	2	0.9697	6.3363	41.24
2,2′,3,4,4′-BDE85	2	1	2	1.5534	6.3363	42.08
3,3′,4,4′,5-BDE126	0	3	2	0.7058	6.3363	42.41
2,3,3′,4,4′-BDE105	1	2	2	1.4619	6.3363	42.65
2,2′,4,4′,6,6′-BDE155	4	0	2	0.7483	6.4671	42.36
2,2′,4,4′,5,6′-BDE154	3	1	2	0.6234	6.4671	43.02
2,2′,4,4′,5,5′-BDE153	2	2	2	0.3542	6.4671	44.11
2,2′,3,4,4′,6′-BDE140	3	1	2	0.9356	6.4671	44.70
2,2′,3,4,4′,5-BDE138	2	2	2	1.0732	6.4671	45.35
2,3,4,4′,5,6-BDE166	2	2	2	0.6766	6.4671	45.35
2,2′,3,4,4′,5′,6-BDE183	3	2	2	1.0773	6.5827	46.74
2,2′,3,4,4′,5,6-BDE181	3	2	2	1.3231	6.5827	47.95
2,3,3′,4,4′,5,6-BDE190	2	3	2	1.0992	6.5827	48.12
2,2′,3,3′,4,5,5′,6,6′-BDE208	4	4	1	0.7966	6.7802	51.92
2,2′,3,3′,4,4′,5,6,6′-BDE207	4	3	2	0.7868	6.7802	52.13
2,2′,3,3′,4,4′,5,5′,6-BDE206	3	4	2	1.1164	6.7802	52.60
2,2′,3,3′,4,4′,5,5′,6,6′-BDE209	4	4	2	0.6199	6.8661	54.81

Table 6
Bromine substitution patterns, semi-empirical MNDO-PM3 method calculated dipole moments, and natural logarithms of the molecular weight for the remaining 163 PBDE congeners for which analytical standards were not available and whose RRT was calculated

	Number of *ortho*-Br	Number of *meta*-Br	Number of *para*-Br	Dipole (Debye)	ln MW
2,2′-BDE4	2	0	0	2.3345	5.7930
2,3-BDE5	1	1	0	2.1760	5.7930
2,3′-BDE6	1	1	0	1.9377	5.7930
2,5-BDE9	1	1	0	1.2445	5.7930
3,5-BDE14	0	2	0	1.5576	5.7930
2,2′,3-BDE16	2	1	0	2.5786	6.0086
2,2′,5-BDE18	2	1	0	1.4632	6.0086
2,2′,6-BDE19	3	0	0	2.4469	6.0086
2,3,3′-BDE20	1	2	0	2.0770	6.0086
2,3,4-BDE21	1	1	1	2.1614	6.0086
2,3,4′-BDE22	1	1	1	1.7934	6.0086
2,3,5-BDE23	1	2	0	1.9595	6.0086
2,3,6-BDE24	2	1	0	1.3691	6.0086
2,3′,5-BDE26	1	2	0	1.6690	6.0086
2,3′,6-BDE27	2	1	0	2.7149	6.0086
2,4,5-BDE29	1	1	1	1.6231	6.0086
2,4′,5-BDE31	1	1	1	1.0770	6.0086
2,3′,5′-BDE34	1	2	0	2.0092	6.0086
3,3′,5-BDE36	0	3	0	1.2804	6.0086
3,4,5-BDE38	0	2	1	1.7427	6.0086
3,4′,5-BDE39	0	2	1	0.1706	6.0086
2,2′,3,3′-BDE40	2	2	0	2.6949	6.1858
2,2′,3,4-BDE41	2	1	1	2.4167	6.1858
2,2′,3,4′-BDE42	2	1	1	2.1622	6.1858
2,2′,3,5-BDE43	2	2	0	1.9004	6.1858
2,2′,3,5′-BDE44	2	2	0	2.2509	6.1858
2,2′,3,6-BDE45	3	1	0	1.8754	6.1858
2,2′,3,6′-BDE46	3	1	0	1.4197	6.1858
2,2′,4,5-BDE48	2	1	1	1.7741	6.1858
2,2′,4,6-BDE50	3	0	1	1.7826	6.1858
2,2′,4,6′-BDE51	3	0	1	1.2989	6.1858
2,2′,5,5′-BDE52	2	2	0	0.3816	6.1858
2,2′,5,6′-BDE53	3	1	0	1.4079	6.1858
2,2′,6,6′-BDE54	4	0	0	1.5765	6.1858
2,3,3′,4-BDE55	1	2	1	1.3971	6.1858
2,3,3′,4′-BDE56	1	2	1	1.6070	6.1858
2,3,3′,5-BDE57	1	3	0	1.4448	6.1858
2,3,3′,5′-BDE58	1	3	0	1.8841	6.1858
2,3,3′,6-BDE59	2	2	0	2.1972	6.1858
2,3,4,4′-BDE60	1	1	2	1.2337	6.1858
2,3,4,5-BDE61	1	2	1	1.7344	6.1858
2,3,4,6-BDE62	2	1	1	1.5143	6.1858
2,3,4′,5-BDE63	1	2	1	0.8685	6.1858
2,3,4′,6-BDE64	2	1	1	1.5845	6.1858
2,3,5,6-BDE65	2	2	0	1.1797	6.1858
2,3′,4,5-BDE67	1	2	1	1.5102	6.1858
2,3′,4,5′-BDE68	1	2	1	1.0901	6.1858
2,3′,4,6-BDE69	2	1	1	1.4201	6.1858
2,3′,4′,5-BDE70	1	2	1	1.5315	6.1858
2,3′,5,5′-BDE72	1	3	0	1.1901	6.1858
2,3′,5′,6-BDE73	2	2	0	2.3009	6.1858
2,4,4′,5-BDE74	1	1	2	0.6007	6.1858
2,3′,4′,5′-BDE76	1	2	1	2.1609	6.1858

Table 6 (*Continued*)

	Number of *ortho*-Br	Number of *meta*-Br	Number of *para*-Br	Dipole (Debye)	ln MW
3,3′,4,5-BDE78	0	3	1	1.3549	6.1858
3,3′,4,5′-BDE79	0	3	1	0.9168	6.1858
3,3′,5,5′-BDE80	0	4	0	0.5743	6.1858
3,4,4′,5-BDE81	0	2	2	0.5410	6.1858
2,2′,3,3′,4-BDE82	2	2	1	2.2485	6.3363
2,2′,3,3′,5-BDE83	2	3	0	1.9213	6.3363
2,2′,3,3′,6-BDE84	3	2	0	2.4508	6.3363
2,2′,3,4,5-BDE86	2	2	1	2.0866	6.3363
2,2′,3,4,5′-BDE87	2	2	1	1.9811	6.3363
2,2′,3,4,6-BDE88	3	1	1	1.7239	6.3363
2,2′,3,4,6′-BDE89	3	1	1	1.6216	6.3363
2,2′,3,4′,5-BDE90	2	2	1	1.2295	6.3363
2,2′,3,4′,6-BDE91	3	1	1	2.0183	6.3363
2,2′,3,5,5′-BDE92	2	3	0	1.5086	6.3363
2,2′,3,5,6-BDE93	3	2	0	1.8475	6.3363
2,2′,3,5,6′-BDE94	3	2	0	1.4284	6.3363
2,2′,3,5′,6-BDE95	3	2	0	1.6098	6.3363
2,2′,3,6,6′-BDE96	4	1	0	1.1971	6.3363
2,2′,3,4′,5′-BDE97	2	2	1	1.9633	6.3363
2,2′,3,4′,6′-BDE98	3	1	1	1.3485	6.3363
2,2′,4,5,6′-BDE102	3	1	1	1.7064	6.3363
2,2′,4,5′,6-BDE103	3	1	1	0.7145	6.3363
2,2′,4,6,6′-BDE104	4	0	1	1.5947	6.3363
2,3,3′,4,5-BDE106	1	3	1	1.3679	6.3363
2,3,3′,4′,5-BDE107	1	3	1	1.0151	6.3363
2,3,3′,4,5′-BDE108	1	3	1	1.3965	6.3363
2,3,3′,4,6-BDE109	2	2	1	1.6731	6.3363
2,3,3′,4′,6-BDE110	2	2	1	2.2296	6.3363
2,3,3′,5,5′-BDE111	1	4	0	1.0195	6.3363
2,3,3′,5,6-BDE112	2	3	0	1.8834	6.3363
2,3,3′,5′,6-BDE113	2	3	0	1.0181	6.3363
2,3,4,4′,5-BDE114	1	2	2	0.7117	6.3363
2,3,4,4′,6-BDE115	2	1	2	0.8907	6.3363
2,3,4′,5,6-BDE117	2	2	1	1.1097	6.3363
2,3′,4,5,5′-BDE120	1	3	1	0.6867	6.3363
2,3′,4,5′,6-BDE121	2	2	1	1.0782	6.3363
2,3,3′,4′,5′-BDE122	1	3	1	2.0089	6.3363
2,3′,4,4′,5′-BDE123	1	2	2	1.1113	6.3363
2,3′,4′,5,5′-BDE124	1	3	1	1.3198	6.3363
2,3′,4′,5′,6-BDE125	2	2	1	2.5796	6.3363
3,3′,4,5,5′-BDE127	0	4	1	0.5565	6.3363
2,2′,3,3′,4,4′-BDE128	2	2	2	1.6828	6.4671
2,2′,3,3′,4,5-BDE129	2	3	1	1.7725	6.4671
2,2′,3,3′,4,5′-BDE130	2	3	1	1.3969	6.4671
2,2′,3,3′,4,6-BDE131	3	2	1	2.0355	6.4671
2,2′,3,3′,4,6′-BDE132	3	2	1	0.9347	6.4671
2,2′,3,3′,5,5′-BDE133	2	4	0	0.8640	6.4671
2,2′,3,3′,5,6-BDE134	3	3	0	2.1494	6.4671
2,2′,3,3′,5,6′-BDE135	3	3	0	0.9384	6.4671
2,2′,3,3′,6,6′-BDE136	4	2	0	0.7992	6.4671
2,2′,3,4,4′,5-BDE137	2	2	2	1.0302	6.4671
2,2′,3,4,4′,6-BDE139	3	1	2	1.5132	6.4671
2,2′,3,4,5,5′-BDE141	2	3	1	1.0945	6.4671
2,2′,3,4,5,6-BDE142	3	2	1	1.7884	6.4671
2,2′,3,4,5,6′-BDE143	3	2	1	1.7345	6.4671

Table 6 (*Continued*)

	Number of *ortho*-Br	Number of *meta*-Br	Number of *para*-Br	Dipole (Debye)	ln MW
2,2′,3,4,5′,6-BDE144	3	2	1	0.6528	6.4671
2,2′,3,4,6,6′-BDE145	4	1	1	1.6083	6.4671
2,2′,3,4′,5,5′-BDE146	2	3	1	1.0983	6.4671
2,2′,3,4′,5,6-BDE147	3	2	1	1.7015	6.4671
2,2′,3,4′,5,6′-BDE148	3	2	1	0.6354	6.4671
2,2′,3,4′,5′,6-BDE149	3	2	1	1.7460	6.4671
2,2′,3,4′,6,6′-BDE150	4	1	1	1.1963	6.4671
2,2′,3,5,5′,6-BDE151	3	3	0	1.0929	6.4671
2,2′,3,5,6,6′-BDE152	4	2	0	1.7463	6.4671
2,3,3′,4,4′,5-BDE156	1	3	2	0.7521	6.4671
2,3,3′,4,4′,5′-BDE157	1	3	2	1.2275	6.4671
2,3,3′,4,4′,6-BDE158	2	2	2	1.5692	6.4671
2,3,3′,4,5,5′-BDE159	1	4	1	0.7538	6.4671
2,3,3′,4,5,6-BDE160	2	3	1	1.5564	6.4671
2,3,3′,4,5′,6-BDE161	2	3	1	1.0323	6.4671
2,3,3′,4′,5,5′-BDE162	1	4	1	1.1860	6.4671
2,3,3′,4′,5,6-BDE163	2	3	1	1.7853	6.4671
2,3,3′,4′,5′,6-BDE164	2	3	1	2.0653	6.4671
2,3,3′,5,5′,6-BDE165	2	4	0	1.1175	6.4671
2,3′,4,4′,5,5′-BDE167	1	3	2	0.7066	6.4671
2,3′,4,4′,5′,6-BDE168	2	2	2	1.3717	6.4671
3,3′,4,4′,5,5′-BDE169	0	4	2	0.3718	6.4671
2,2′,3,3′,4,4′,5-BDE170	2	3	2	1.2177	6.5827
2,2′,3,3′,4,4′,6-BDE171	3	2	2	1.8958	6.5827
2,2′,3,3′,4,5,5′-BDE172	2	4	1	0.8027	6.5827
2,2′,3,3′,4,5,6-BDE173	3	3	1	1.8675	6.5827
2,2′,3,3′,4,5,6′-BDE174	3	3	1	1.1409	6.5827
2,2′,3,3′,4,5′,6-BDE175	3	3	1	1.1943	6.5827
2,2′,3,3′,4,6,6′-BDE176	4	2	1	0.8688	6.5827
2,2′,3,3′,4,5′,6′-BDE177	3	3	1	0.6716	6.5827
2,2′,3,3′,5,5′,6-BDE178	3	4	0	1.3743	6.5827
2,2′,3,3′,5,6,6′-BDE179	4	3	0	0.9946	6.5827
2,2′,3,4,4′,5,5′-BDE180	2	3	2	0.5002	6.5827
2,2′,3,4,4′,5,6′-BDE182	3	2	2	0.5259	6.5827
2,2,3,4,4′,6,6′-BDE184	4	1	2	0.5726	6.5827
2,2′,3,4,5,5′,6-BDE185	3	3	1	0.6494	6.5827
2,2′,3,4,5,6,6′-BDE186	4	2	1	1.7559	6.5827
2,2′,3,4′,5,5′,6-BDE187	3	3	1	1.2024	6.5827
2,2′,3,4′,5,6,6′-BDE188	4	2	1	0.8475	6.5827
2,3,3′,4,4′,5,5′-BDE189	1	4	2	0.6731	6.5827
2,3,3′,4,4′,5′,6-BDE191	2	3	2	1.2750	6.5827
2,3,3′,4,5,5′,6-BDE192	2	4	1	0.9045	6.5827
2,3,3′,4′,5,5′,6-BDE193	2	4	1	1.4465	6.5827
2,2′,3,3′,4,4′,5,5′-BDE194	2	4	2	0.7064	6.6863
2,2′,3,3′,4,4′,5,6-BDE195	3	3	2	1.6021	6.6863
2,2′,3,3′,4,4′,5,6′-BDE196	3	3	2	0.3595	6.6863
2,2′,3,3′,4,4′,6,6′-BDE197	4	2	2	0.3479	6.6863
2,2′,3,3′,4,5,5′,6-BDE198	3	4	1	0.9791	6.6863
2,2′,3,3′,4,5,5′,6′-BDE199	3	4	1	0.6463	6.6863
2,2′,3,3′,4,5,6,6′-BDE200	4	3	1	1.1814	6.6863
2,2′,3,3′,4,5′,6,6′-BDE201	4	3	1	0.6565	6.6863
2,2′,3,3′,5,5′,6,6′-BDE202	4	4	0	0.8725	6.6863
2,2′,3,4,4′,5,5′,6-BDE203	3	3	2	0.7553	6.6863
2,2′,3,4,4′,5,6,6′-BDE204	4	2	2	0.6434	6.6863
2,3,3′,4,4′,5,5′,6-BDE205	2	4	2	0.9480	6.6863

as they may "round out" the identification of nearly all environmental relevant PBDE congeners with concentrations greater than the 0.1–1 pg/g detection limits. Such an approach to narrowing the potential synthetic field using readily available retention time models can immediately reduce the immediate synthetic requirements by ∼50% (i.e. from 163 potential congeners to 84). Further refinements in both GC retention time models and detailed examinations of the mass spectral fragmentation patterns for PBDEs should further reduce this number. The large number of potential congener identities for several of the penta- and hexa-brominated unknowns also attests to the chromatographic congestion for these homologue groups. Hence, full congener resolution and reliable quantitation of all 209 PBDEs on a single column may either require significant advances in column materials and instrumental programming, or simply may not be possible. As well, our group is currently examining photochemical debromination techniques of higher brominated congeners as a means of "photo-synthesizing" unknown congeners through judicious choice of potential debromination pathways (i.e. only a select group of debrominated congeners may be formed from a parent congener, and choosing systems where the debromination products have substantially different predicted RRTs facilitates more certain structural identification). In combination with these potential unknown identities using environmental samples, such RRT models coupled with novel "synthetic" routes offer potential to help identify the ∼80% of currently unknown PBDE congeners potentially residing in environmental matrices that may be of toxicological concern.

4. Supplementary materials

Bromine substitution patterns, semi-empirical MNDO-PM3 method calculated dipole moments, natural logarithms of the molecular weight, and observed retention times for the 46 PBDE congeners used in constructing the RRT model are given in Table 5 while the bromine substitution patterns, semi-empirical MNDO-PM3 method calculated dipole moments, and natural logarithms of the molecular weight for the remaining 163 PBDE congeners for which analytical standards were not available and whose RRT was calculated are given in Table 6.

Acknowledgements

We thank Maike Fischer for assistance with the HRGC/HRMS experiments, Paula Sather for assistance with the 1/2-RRT model, and the Department of Fisheries and Oceans (Canada) for providing the opportunity to collaborate on this project.

References

[1] R. Renner, Environ. Sci. Technol. 34 (2000) 222a.
[2] J. de Boer, in: J. Paasivirta (Ed.), The Handbook of Environmental Chemistry. Part K. New Types of Persistent Halogenated Compounds, Springer-Verlag, Berlin, 2000.
[3] M.G. Ikonomou, S. Rayne, M. Fischer, M.P. Fernandez, W. Cretney, Chemosphere 46 (2002) 649.
[4] M.G. Ikonomou, S. Rayne, R.F. Addison, Environ. Sci. Technol. 36 (2002) 1886.
[5] S. Rayne, M.G. Ikonomou, B. Antcliffe, Environ. Sci. Technol. 37 (2003) 2847.
[6] F. Rahman, K.H. Langford, M.D. Scrimshaw, J.N. Lester, Sci. Total Environ. 275 (2001) 1.
[7] A.M.C.M. Pijnenburg, J.W. Everts, J. de Boer, J.P. Boon, Rev. Environ. Contam. Toxicol. 141 (1995) 1.
[8] S. Rayne, M.G. Ikonomou, Anal. Chem. 75 (2003) 1049.
[9] M.G. Ikonomou, S. Rayne, Anal. Chem. 74 (2002) 5263.
[10] S. Rayne, M.G. Ikonomou, Environ. Toxicol. Chem. 21 (2002) 2292.
[11] S. Rayne, M.G. Ikonomou, M.D. Whale, Water Res. 37 (2003) 551.
[12] T. Nevalainen, J. Koistinen, P. Nurmela, Environ. Sci. Technol. 28 (1994) 1341.
[13] E.K. Whalen-Pedersen, P.C. Jurs, Anal. Chem. 53 (1981) 2184.
[14] V.S. Ong, R.A. Hites, Anal. Chem. 63 (1991) 2829.
[15] A. Bemgard, A. Colmsjo, K. Wrangskog, Anal. Chem. 66 (1994) 4288.
[16] M.D. Hale, F.D. Hileman, T. Mazer, T.L. Shell, R.W. Noble, J.J. Brooks, Anal. Chem. 57 (1985) 640.
[17] M.N. Hasan, P.C. Jurs, Anal. Chem. 60 (1988) 978.
[18] A. Robbat, G. Xyrafas, D. Marshall, Anal. Chem. 60 (1988) 982.