PROFILES OF SEVEN BROMINATED DIPHENYL ETHERS (BDEs) IN AQUATIC BIOTA FROM THE BALTIC SEA AND GREAT LAKES

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Introduction

The number of polybrominated diphenyl ethers, measured in aquatic fauna by different laboratories, varies from 4 or 5 to 31 (see examples in Table 1). Roots et al. [1] reviewed the profiles of the five most frequently reported BDEs (2,2',4,4'-tetra (BDE47), 2,2',4,4',6-penta (BDE100), 2,2',4,4',5-penta (BDE99), 2,2',4,4',5,6'-hexa(BDE154), and 2,2',4,4',5,5'-hexabromo diphenyl ether (BDE153), and of seven BDEs (5 mentioned above + 2,4,4'-tribromo diphenyl ether (BDE 28) and 2,3',4,4'-tetrabromo diphenyl ether (BDE66)) reported by three laboratories [1,8,9] The profiles vary a great deal. Even the profiles of only four BDEs (47, 99,100, and 153), reported by two of these laboratories for the same fish species from the Great Lakes are different. This suggests the possibility of a systematic difference. Another four laboratories ([10], [12]-[14]) reported the seven BDEs above, since the review [1]. This paper compares the reports of these seven laboratories. The examination was carried out by Principal Component Analysis (PCA), as described [1].

The results of PCA are score plots, which show the similarities of the sample profiles in new coordinates – principal components, and loading plots, which show the effects of the BDEs on the principal components. With its visualizing capability, PCA is a convenient quality control tool and its score and loading plots should be used early during the project so that potential errors or'outliers' can be detected and the samples reanalyzed, if necessary.

Material and methods

The examination of the profies was performed by PCA, which allows visual inspection of the multi-dimensional data by projecting them on planes principal components (see for example [1]).

Results and discussion:

The projections on the planes of the principal components show that the profiles form clusters related to the origin of and species of marine fauna in samples. Unfortunately, it is not possible to tell to what extent the differences among the laboratories are due to analytical procedures and to what extent to regional and species differences. The data from Baltic fish [1], farmed and wild salmon from North America [10], and fish from the Great Lakes [8] are in an approximately central cluster, although the latter contain a few outliers.Under the central cluster is a cluster of BDE profiles of crustaceans, reported by Bodin et al.[9]. Crustaceans' metabolic capability usually differs from that of fish and may be in part responsible for the slightly different position of this cluster. The samples of fish from markets and supermarkets in south China [12] form a cluster far removed from that of fish from Hong Kong markets [13]. The difference in the positions of these two clusters is caused the difference in the fractions of the BDE47 and BDE99 (Table 2). Most of the BDE profiles in samples of eels from the coastal north-western Mediterranean Sea [14] contain relatively high fractions of BDE153 and BDE154. Figure 2 shows the presence of two 'outliers', one because of an unusually high fraction of BDE 28 [14], the other because of an unusually high fraction of BDE66[13] (see the loading plot, Figure 4). The effect of individual BDEs on the principal components can be seen from the loading plots (Figures 1 & 2). It is of interest to compare individually the loading plots of the profiles obtained by different laboratories .If the relations among the BDEs are similar, so should be the loading plots. Figure 3 shows that there are considerable differences in the BDE profiles reported by the laboratories. The major BDEs, BDE47 and BDE99 have the most consistent pattern, whereas the other BDEs are scattered. Considering the relative stability of these compounds, it appears that this scatter is caused primarily by analytical uncertainties.

Conclusion remarks

The variations of the BDE analyses reported by different laboratories have not diminished since the previous review [1] and systematic differences among the laboratories may still exist. It should be a

standard practice to report the results of the analyses of a generally available 'BDE in a biological matrix' reference material Several intercomparison exercises have been reported [15]. The relative standard deviations between laboratories were 17- 40% for BDEs in biological matrices, and 22 – 60% in a polymer matrix.

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Table 1: Example of polybrominated diphenyl ethers, measured in aquatic fauna *

	Ref	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	BDE															
1	3														X	
2	7														X	
3	15								X						X	
4	17									X	X				X	X
5	28	X	X	X				X	X	X	X	X	X	X	X	X
6	75	X	X													
7	47	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
8	49									X					X	X
9	66	X	X							X	X	X		X	X	X
10	71	X	X		X					X	X				X	X
11	77	X	X												X	X
12	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
13	119	X	X													
14	99	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
15	85	X	X		X					X	X	X			X	X
16	119														X	
17	126														X	
18	154	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
19	153	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
20	138	X	X		X					X	X	X		X	X	
21	156														X	
22	183	X	X					X	X	X	X		X	X	X	
23	184														X	
24	190	X	X							X	X					
25	191														X	
26	196								X							
27	197								X							
28	206								X				X			
29	207								X				X			
30	208												X			
31	209	X	X						X				X	X		

*Studies [1],[8][10], and [12]-[14] were used in this paper

Table 2. Average BDE profiles in the examined data

BDE->	28	47	66	100	99	153	154
Ref [1]	3.31	60.18	3.17	11.79	12.97	3.14	5.44
[8]	1.88	53.32	2.06	12.38	17.38	5.02	7.96
[9]	4.32	61.34	0.21	10.02	17.85	4.03	2.23
[10]	2.57	57.94	3.18	12.07	13.29	6.00	4.96
[12]	10.00	58.51	4.59	8.62	6.00	3.58	8.71
[13]	2.74	33.52	3.25	18.64	35.01	3.20	3.65
[14]	10.96	38.58	4.62	12.61	6.35	15.95	10.93

Figure 1: Loading plot – the effect of BDEs on the principal components pc-1 (ev-1) and pc-2 (ev-2)

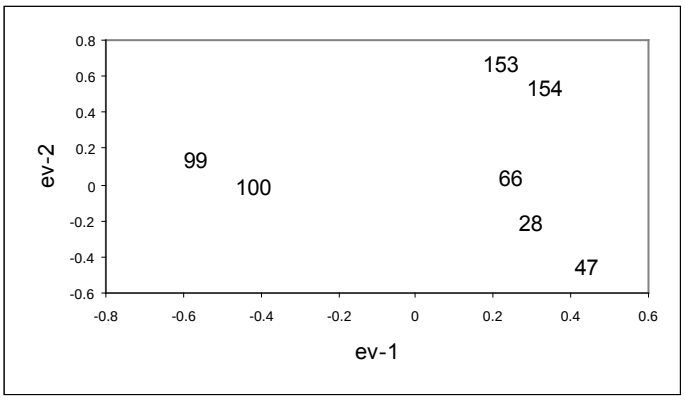


Figure 2: Loading plot – the effect of BDEs on the principal components pc-1 (ev-1) and pc-3 (ev-3)

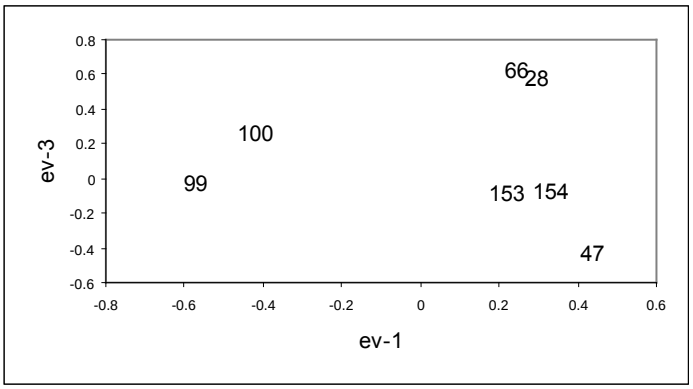
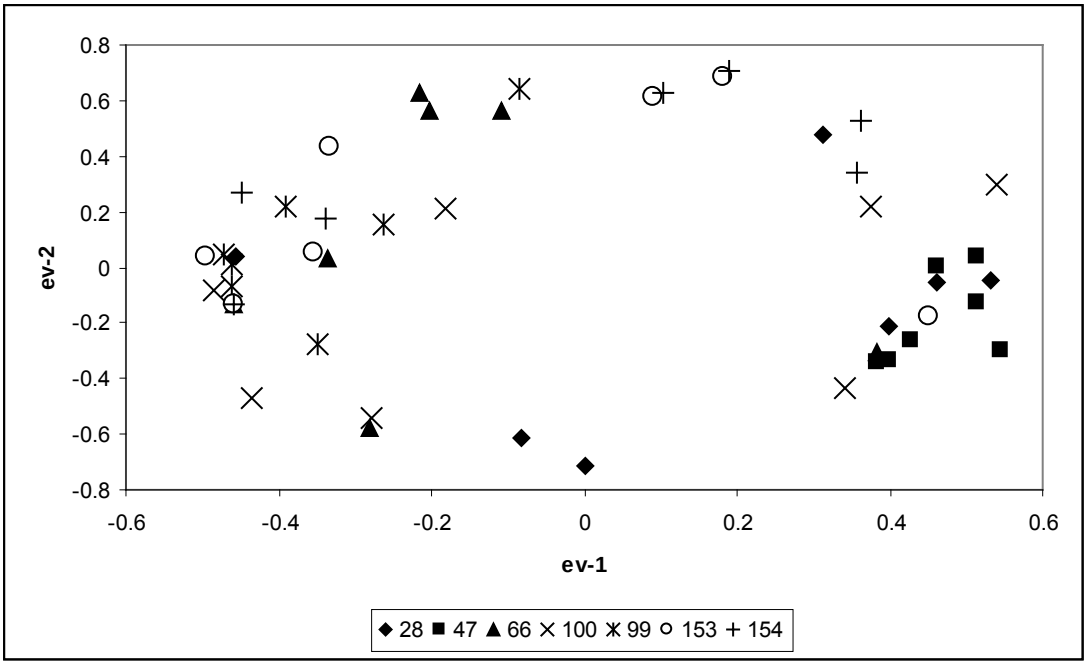


Figure 3: Individual loading plots ev-1 & ev-2 obtained by the different laboratories.


0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
ev-2
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
ev-1
28 47 66 100 99 153 154