Organohalogen Compounds, Volume 61, Pages 135-138 (2003)

POLYBROMINATED DIPHENYL ETHERS IN LIVER AND MUSCLE TISSUE OF FRESHWATER FISH FROM GERMANY

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Introduction

Brominated flame retardants are added to a wide range of materials, including plastics, textiles and polyurethane foam, at concentrations up to 30% by weight in order to prevent them from catching fire. In environmental studies the major emphasis to date has been on the polybrominated diphenyl ethers (PBDEs), and in particular those congeners, which derive from technical penta-mix formulation. These compounds have now been detected in all environmental compartments including Arctic fish and marine mammals[1,2]. Comprehensive risk assessments have been conducted for BDE formulations within the European Union, which concluded as a consequence of the identified risk that penta- and octaBDE should be prohibited[3-5]. Furthermore, BDEs were included in the list of priority substances in the field of water policy and hence they have to be monitored in the aquatic environment regularly on European scale[6]. Present-day information on the BDE contamination level of aquatic ecosystems in Germany are scarce for both tetra- to hexabromodiphenyl ethers and higher brominated congeners. In a recent study total BDE concentrations of 26 to 728 ng/g (lw) in bream and eel samples from the river Elbe were reported[7].

In this paper we report the concentrations of BDEs in liver and muscle tissue of three freshwater fish species sampled in the river Elbe and two of its tributaries in Germany.

Materials and Methods

Eel (*Anguilla anguilla L.*), pike-perch (*Stizostedion lucioperca L.*) and bream (*Abramis brama L.*) samples were collected in 2001 during a fish species survey in the river Elbe upstream the city of Dresden and in two of its tributaries Stoer and Oste, which meet the river Elbe near Hamburg. After taking biometric data (weight, length) muscle tissue and livers were extracted, homogenized and stored frozen until analysis for PBDEs. A modified analytical procedure described previously was employed[7]. In brief, 10 to 30 g of muscle tissue or 3 to 6 g of liver tissue representing 0.3 to 1.0 g of lipid were dried with sodium sulphate and soxhlet extracted for 16 hours with toluene. The obtained lipid fraction was cleaned-up by multi-layer column chromatography (silica gel, alkaline- and acid-impregnated silica gel) and gel permeation chromatography. Quantification of BDEs 28, 47, 66, 71, 75, 85, 99, 100, 138, 153, 154, 183, 190 and 209 was performed by capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC-ECNI-MS) in the selected ion monitoring mode under the following conditions: GC 6890+ / MSD 5973 (Agilent, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Switzerland) and PTV injector KAS 4 plus (Gerstel, Germany); capillary column: Rtx-CLPesticides (Restek, U.S.A.), 30 m x 0.25 mm, film thickness: 0.25 µm; pressure-pulse injection, injection volume: 2µl; carrier gas: helium; CI ion source, reagent gas: methane; ion source temperature: 210°C. BDEs elute from the column under these conditions between 11 and 35 minutes. For congeners with three to seven

bromine atoms the most prominent ions due to bromine at m/z = 79 and m/z = 81 were recorded, while for the decabromodiphenyl ether (BDE209) the highly specific ions at m/z = 484.7 and m/z = 486.7 were monitored. BDE77, 116, 140, 181 (never found in environmental samples), ^{13}C-labelled BDE209 and BB209 were used as internal standards and syringe standard, respectively. All standards were purchased from Promochem (Wesel, Germany) and Greyhound chromatography (Birkenhead, U.K.), respectively.

Results and Discussion

Lipid-normalised (lw) and wet weight (ww) based concentrations of BDE28, 47, 100, 99, 154, 153 and sum of tri- to hexabrominated congeners in liver and muscle tissue of pike-perch (*Stizostedion lucioperca L.*), eel (*Anguilla anguilla L.*) and bream (*Abramis brama L.*) are summarised in tables 1-3 with information on median, minimum and maximum concentration. Other congeners were largely found at low levels or were below the limits of quantification (LOQ). From the data in Table 1-3 can be concluded that there are no significant differences in concentrations of BDEs in muscle and liver tissue within a particular species when data were normalised on lipid content. This denotes that both matrices might be used for monitoring purposes. Moreover, the ranges of BDE-concentrations found in fish samples collected in particular river sections are quite close indicating diffuse input of PBDEs, only. This corresponds to the fact that the ecological quality of the rivers Oste and Stoer in the northern German plain is considered as good. There are no industries, which might be suspected to discharge PBDEs into the two rivers. Mean BDE47 concentration in bream from the river Oste was 2.45 ± 0.25 ng/g dry weight (dw) assuming an average dry weight of 22%. This concentration is clearly lower than those reported recently in bream from the Netherlands (0.2-130 ng/g dw)[8] and the river Elbe near the city of Dresden, Germany (0.9-62 ng/g dw)[7]. Total BDE levels in livers of eel from the river Elbe and its tributary Stör were in the same range (20.0-129.4 ng/g lw and 40-100.5 ng/g lw), respectively but much lower than concentrations found in eels from Dutch rivers and lakes[9]. All three fish species showed BDE profiles dominated by BDE47 (Fig. 1). BDE99 present in technical penta formulations at the same level[10] as BDE47 was found in bream and eel at low concentrations only whilst in peak-perch the concentration was much higher. The percentage of BDE100 in muscle tissue of different freshwater fish species was of the same order as in the technical penta-mix whilst in liver samples it seemed to be even higher. In marine fish species (herring, cod, whiting, sole)[1,11,12], invertebrates (sea star, hermit crab, whelk, shrimp, crab, blue mussel)[1,11] and mammals (harbour porpoise, harbour seal, ringed seal)[1,11,12] the contribution of BDE99 and BDE100 to the total BDE content is similar or the percentage of BDE99 is even higher than that of BDE100, respectively. These differences in congener pattern can be explained by a high bio-transformation capacity of bream and eel for BDE99 or a limited uptake of this congener by these species. Other freshwater species e.g. rainbow trout, whitefish (*Coregonus sp.*), flathead catfish, channel catfish show similar BDE profiles as marine species[13,14], but not carp[14]. This observation is in agreement with a dietary uptake study in carp, where no accumulation of BDE-99 was detected in the exposed fish[15]. Obviously, congener pattern vary considerably between fish species and caution is needed when extrapolating results from one species to the other.

Acknowledgements

This work was funded in part by the German Federal Ministry of Education and Research and the Deutsche Forschungsgemeinschaft. The authors thank Burkhard Stachel (Wasserguetestelle Elbe) for providing the fish samples.

Table 1. Concentrations (ng/g lw and ng/g ww) of most often detected BDE congeners in muscle and liver tissue of pike-perch and eel collected in the river Stör, a small tributary of the river Elbe north of Hamburg, Germany. LOQ = limit of quantification.

	BDE28	**BDE47**	**BDE100**	**BDE99**	**BDE154**	**BDE153**	**∑ Penta**
Species	Pike-perch (*Stizostedion lucioperca L.*) - Muscle tissue (n=9)						
Median	<LOQ	83.5/0.52	16.1/0.09	11.8/0.07	0.7/0.005	6.8/0.04	145.4/0.72
Min	<LOQ	37.2/0.21	5.9/0.03	7.2/0.04	<LOQ	2.9/0.02	54.7/0.31
Max	1.9/0.01	140.1/0.62	25.0/0.12	28.6/0.18	2.50.02	12.2/0.06	192.2/0.96
Species	Pike-perch (*Stizostedion lucioperca L.*) - Liver (n=9)						
Median	1.3/0.06	68.8/3.35	12.1/0.52	16.4/0.85	3.4/0.14	2.4/0.10	110.0/4.73
Min	<LOQ	38.8/1.73	7.2/0.33	7.6/0.29	0.9/0.03	1.3/0.06	59.2/2.64
Max	2.6/0.13	145.0/7.73	34.0/2.02	41.5/3.02	13.3/0.72	10.40.57	224.5/13.91
Species	Eel (*Anguilla anguilla L*). - Liver (n=9)						
Median	0.4/0.02	35.5/1.65	22.6/1.63	0.4/0.04	1.0/0.05	0.7/0.03	62.9/3.19
Min	<LOQ	12.9/0.65	9.5/0.45	<LOQ	0.4/0.02	0.4/0.02	39.6/2.18
Max	3.4/0.17	57.6/4.00	37.8/1.91	2.5/0.13	1.5/0.09	2.2/0.14	100.5/5.75

Table 2. Concentrations (ng/g lw and ng/g ww) of most often detected BDE congeners in muscle and liver tissue of eel collected in the river Elbe, Germany near the Czech border. LOQ = limit of quantification.

	BDE28	**BDE47**	**BDE100**	**BDE99**	**BDE154**	**BDE153**	**∑ Penta**
Species	Eel (*Anguilla anguilla L.*) - Muscle tissue (n=8)						
Median	0.4/0.11	22.6/ 7.31	5.7/1.57	1.1/0.28	1.5/0.41	0.8/0.23	33.6/10.05
Min	0.3/0.08	15.3/3.66	3.2/0.76	0.3/0.09	1.1/0.25	0.5/0.14	22.0/5.28
Max	1.2/0.18	54.9/9.69	9.6/2.20	1.6/0.43	2.8/0.75	2.0/0.37	71.6/13.30
Species	Eel (*Anguilla anguilla L).* - Liver (n=19)						
Median	0.1/0.01	21.4/1.80	7.6/0.64	0.6/0.05	1.0/0.09	0.7/0.06	29.0/2.65
Min	<LOQ	12.7/1.02	4.3/0.32	<LOQ	<LOQ	<LOQ	20.0/1.49
Max	1.5/0.09	101.6/6.00	23.2/1.68	3.1/0.23	2.8/0.25	1.7/0.17	129.4/7.71

Table 3. Concentrations (ng/g lw and ng/g ww) of most often detected BDE congeners in muscle and liver tissue of bream collected in the river Oste, a small tributary of the river Elbe southwest of Hamburg, Germany. LOQ = limit of quantification.

	BDE28	**BDE47**	**BDE100**	**BDE99**	**BDE154**	**BDE153**	**∑ Penta**
Species	Bream (*Abrama brama L.*) - Muscle tissue (n=4)						
Median	<LOQ	22.3/0.54	6.3/0.15	0.2/0.01	2.5/0.06	1.1/0.03	33.5/0.80
Min	<LOQ	19.2/0.48	5.5/0.14	0.2/0.002	2.2/0.06	0.7/0.02	28.2/0.70
Max	2.4/0.07	55.5/0.60	16.2/0.17	0.5/0.01	7.5/0.08	2.4/0.03	81.7/0.91
Species	Bream (*Abrama brama L.*) - Liver (n=4)						
Median	<LOQ	18.4/1.20	4.9/0.37	0.3/0.02	2.3/0.16	0.8/0.06	26.4/1.77
Min	<LOQ	16.5/0.66	4.6/0.31	<LOQ	1.6/0.10	0.4/0.04	24.3/1.18
Max	<LOQ	20.4/4.19	10.9/0.97	0.5/0.03	3.1/0.40	1.2/0.08	35.4/5.67

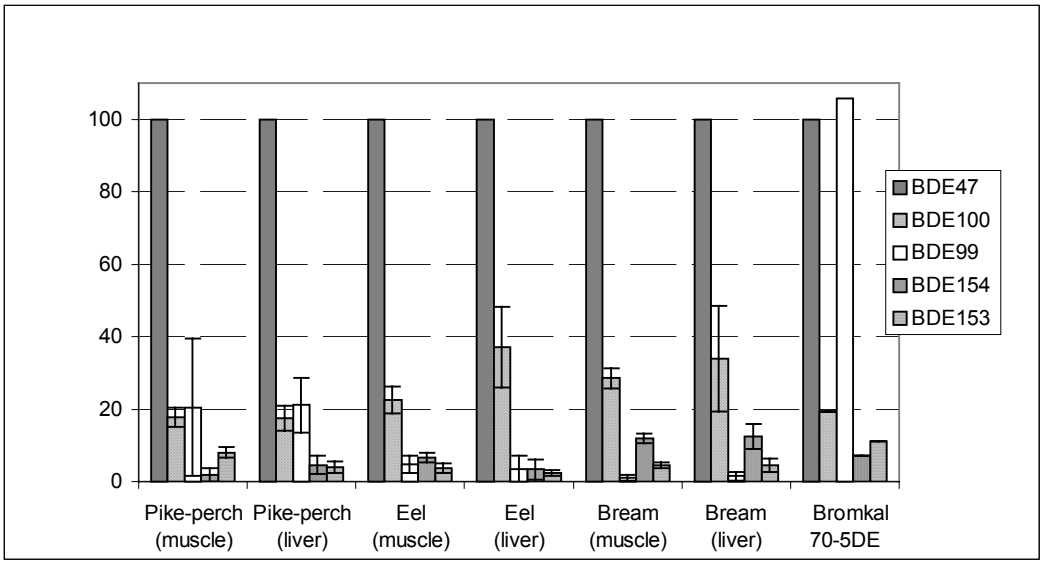

Figure 1. PBDE pattern in different freshwater fish species and in the technical formulation Bromkal 70-5DE. Concentrations of individual congeners were normalised to that of BDE47, mean of n measurements ± standard deviation (pike-perch: muscle/liver n=7/7; eel: muscle/liver n=9/18; bream muscle/liver n=4/4).

References

1. Christensen J.H., Glasius M., Pécseli M., Platz J. and Pritzl G.; (2002) Chemosphere. 47, 631
2. Ikonomou M.G., Rayne S. and Addison R.F.; (2002) Environ Sci Technol. 36, 1886
3. EUR 19730 - European Union Risk Assessment Report, Diphenylether, pentabromo derivative, (2001) 5, 282 pp., Luxembourg
4. EUR 20403 EN - European Union Risk Assessment Report, Diphenylether, octabromo derivative, (2002), 262 pp., Luxembourg
5. EUR 20402 EN - European Union Risk Assessment Report, Bis(pentabromophenyl)ether (2002), 17, 282 pp., Luxembourg
6. Official Journal of the European Union (2001), L331, 1
7. Lepom P., Karasyova T. and Sawal G.; (2002) Organohalogen Compd. 58, 209
8. de Boer J., Wester P.G, van der Horst A. and Leonards P.E.G.; (2003) Environ Poll. 122, 63
9. de Boer J.; (1990) Organohalogen Compd. 2, 315
10. Sjödin A., Jakobsson E., Kierkegaard A., Marsh G. and Sellström U.; (1998) J Chromatogr A. 822, 83
11. Boon J.P., Lewis W.E., Tjoen-a-choi M.R., Allchin C.R., Law R.J., deBoer J., ten Hallers-Tjabbes C.C. and Zegers B.N.; (2002) Environ Sci Technol. 36, 4025
12. Ikonomou M.G., Rayne S., Fischer M., Fernandez M.P. and Cretney W.; Chemosphere. (2002), 46, 649
13. Zenneg M., Kohler M., Gerecke A.C. and Schmid P. (2002), Chemosphere. 51, 545
14. Hale R.C., La Guardia M.J., Harvey E.P., Matteson Mainor T., Duff W.H.; Gaylor M.O.; (2001) Environ Sci Technol. 35, 4585
15. Stapleton H.M., Letcher R.J. and Baker J.E. Organohalogen Compd. (2002) 58, 201