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Brominated flame retardants and related chlorinated persistent organic pollutants in fish from river Elbe and its main tributary Vltava

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Abstract

Brominated flame retardants (BFRs) are widely used industrial chemicals, residues of which can be nowadays found in all environmental compartments. The widespread presence of BFRs in various environmental compartments and food chain is a consequence of both their broad application area and physico-chemical properties, such as resistance to degradation and high lipophilicity. Alike in the case of other halogenated persistent organic pollutants (POPs), fish can be used as a bioindicator of aquatic environment pollution. In presented study, conducted in the year 2005, altogether 80 samples representing the most abundant fresh water fish species, viz. chub (*Leuciscus cephalus*), bream (*Abramis brama*), and perch (*Perca fluviatilis*) collected in 11 sampling sites located at Elbe and Vltava (Moldau) rivers were examined for levels of major BFRs. Without any exception, BFRs were detected in all fish samples. BDE 47 was the dominating congener in all fish species. This fact was not surprising, since it used to be the main component in various kinds of technical mixtures. With regard to relatively high levels of BDE 47 in fish tissue, as compared to other BFRs, and considering strong correlation with the total PBDEs content, simplified laboratory examination and, consequently, increased samples throughput can be obtained when only this congener is monitored. The potential of comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOFMS), to provide more comprehensive information on the bioaccumulating chemicals occurring in fish samples, has been demonstrated in this study.

Keywords: Brominated flame retardants; Polybrominated diphenyl ethers; Hexabromocyclododecane; Comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry; Fish

1. Introduction

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), are widely used industrial chemicals added to various materials important in manufacture of electronic equipment, upholstered furniture, construction materials, textiles to minimise or even suppress the combustion process. BFRs interfere with it at various stages, e.g. during heating, decomposition, ignition, or flame spread and prevent the spread of fires or delay the time of flashover so that people can escape (de Wit, 2002; Sjödin et al., 2003). Thus given the ubiquity of plastics in the modern world, it is not surprising that PBDEs are being found in all environmental compartments, including aquatic ecosystem (Allchin et al., 1999; de Wit, 2002; de Boer et al., 2003; Sjödin et al., 2003). Not only the capacity of PBDEs to bioaccumulate in biotic fatty tissues and biomagnify up the food chain (several studies demonstrated their occurrence in wildlife and human tissue) in combination with

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their resistance to degradation, but also their toxicity make this class of chemicals of a high concern to the environment and human health (de Boer et al., 2000; Rahman et al., 2001; de Wit, 2002; Sjödin et al., 2003). BFRs can cause developmental effects, endocrine disruption, immunotoxicity, reproductive, and long term effects, including second generation effects (Meerts et al., 2000; Darnerud et al., 2001; Eriksson et al., 2001; Birnbaum and Staskal, 2004). With regards to all the hazards posed by penta-BDE and octa-BDE mixtures both these chemicals were banned in the European Union and the United States (www.bsef.com).

River pollution caused by the direct and indirect discharges of both urban and industrial waste, has led to the occurrence of various persistent organic pollutants (POPs), including BFRs that are associated not only with sediment but are transferred also into biota. To assess the amount of biologically available, in addition to chemical water analysis (that is a primarily tool), also bioindicators such as fish are useful for estimation of pollution extents. Fish can be found everywhere in the aquatic environment playing a major ecological role in the aquatic food-webs because of their function as a carrier of energy from lower to higher trophic levels (van der Oost et al., 2003; Lacorte et al., 2006; Pulkrabová et al., in press).

The presented study was focused on the monitoring and the assessment of the time trends in extent and character of pollution of two main Czech rivers, Elbe and Vltava, by most widely used BFRs, viz. PBDEs and HBCD. Their occurrence in Czech aquatic ecosystem was for the first time documented in a pilot study conducted in years 2001–2003 (Pulkrabová et al., in press). Three most common fish species inhabiting monitored localities were employed as pollution bioindicators. The potential of a novel analytical technique represented by comprehensive two-dimensional gas chromatography coupled to a high-speed time-of-flight mass analyser (GC × GC–TOFMS) to generate comprehensive information on the whole spectrum of halogenated POPs in fish extract has been demonstrated.

2. Experimental

2.1. Sample collection

Three sets of fish species representing various trophic levels chub (*Leuciscus cephalus*), bream (*Abramis brama*), and perch (*Perca fluvialis*) were caught during summer and autumn 2005 at 11 sampling sites located at two main Czech rivers: Vltava and Elbe (see Fig. 1). Both unpolluted rural areas and those highly industrialised (near potential emission sources) were sampled. Altogether 80 samples (pooled) were analysed. Skin-free muscle tissues (2–7 individual fillets) corresponding to individual fish species were pooled together in all sampling sites. Lipid content was determined in each composite sample. All samples were kept at −18 °C after pooling and homogenisation.

2.2. Chemicals

Individual standards of PBDE congeners (all with declared purity ⩾99%) were obtained from Cambridge Isotope Laboratories (CIL, USA). Working standard solution in isooctane containing following congeners: 2,4,4′-triBDE (BDE 28), 2,2′,4,4′-tetraBDE (BDE 47), 2,2′,4,5′-tetraBDE (BDE 49), 2,3′,4,4′-tetraBDE (BDE 66), 2,2′,3,4,4′-penta-BDE (BDE 85), 2,2′,4,4′,5-penta-BDE (BDE 99), 2,2′,4,4′,6-penta-BDE (BDE 100), 2,2′,4,4′,5,5′-hexa-BDE (BDE 153), 2,24′,45′,6′-hexaBDE (BDE 154), and 2,2′,4,4′,5′,6-hexa-BDE (BDE 183) were stored in the refrigerator (5 °C). The α-HBCD standard with a declared purity of 98% was also supplied by CIL. Standard of PCB 112 (recovery standard) was purchased from Dr. Ehrenstorfer GmbH (Germany).

Hexane, cyclohexane, and isooctane were supplied by Merck (Germany). Ethyl acetate and dichloromethane were supplied by Scharlau (Spain). All solvents were of "organic trace analysis" grade. Anhydrous sodium sulphate obtained from Penta Chrudim (Czech Republic) was heated at 600 °C for 5 h and then stored in an exsiccator before the use. Styrene-divinylbenzene gel (Bio-Beads S-X3, 200–400 mesh) was purchased from Bio Rad (USA). Sulphuric acid (98%) was obtained from Merck (Germany).

2.3. Analytical method

2.3.1. Extraction of fish

Fish muscle sample homogenate was mixed with anhydrous sodium sulphate to a form of flowing powder. Sample was then transferred into a cellulose extraction thimble and stored in an exsiccator for 12 h to complete dehydration of sample. The thimble was then inserted into a Soxhlet apparatus and extracted for 8 h by a solvent mixture consisting of hexane–dichloromethane (1:1, v/v). The crude extract was carefully evaporated by a rotary vacuum evaporator and the residual solvents were removed by a gentle stream of nitrogen. The lipid content was determined gravimetrically.

2.3.2. Clean-up

An automated gel permeation chromatography (GPC) system consisting of a 350 MASTER pump, a fraction collector, an automatic regulator of loop XLI, a microcomputer (software 731 PC via RS32C), a dilutor 402 (Gilson, France) and a stainless steel column 500 × 8 mm i.d. packed with Bio-Beads S-X3® was employed for purification of the crude extracts. Extracted lipids were dissolved in a solvent mixture of cyclohexane–ethyl acetate (1:1, v/v) containing 5 ng ml^{-1} PCB 112 (this congener is not present either in commercial mixtures or in the environmental samples) employed as a recovery standard. The mobile phase was cyclohexane–ethyl acetate (1:1, v/v). Fraction corresponding to a elution volume of 14–30 ml was collected. The eluate was evaporated by a rotary

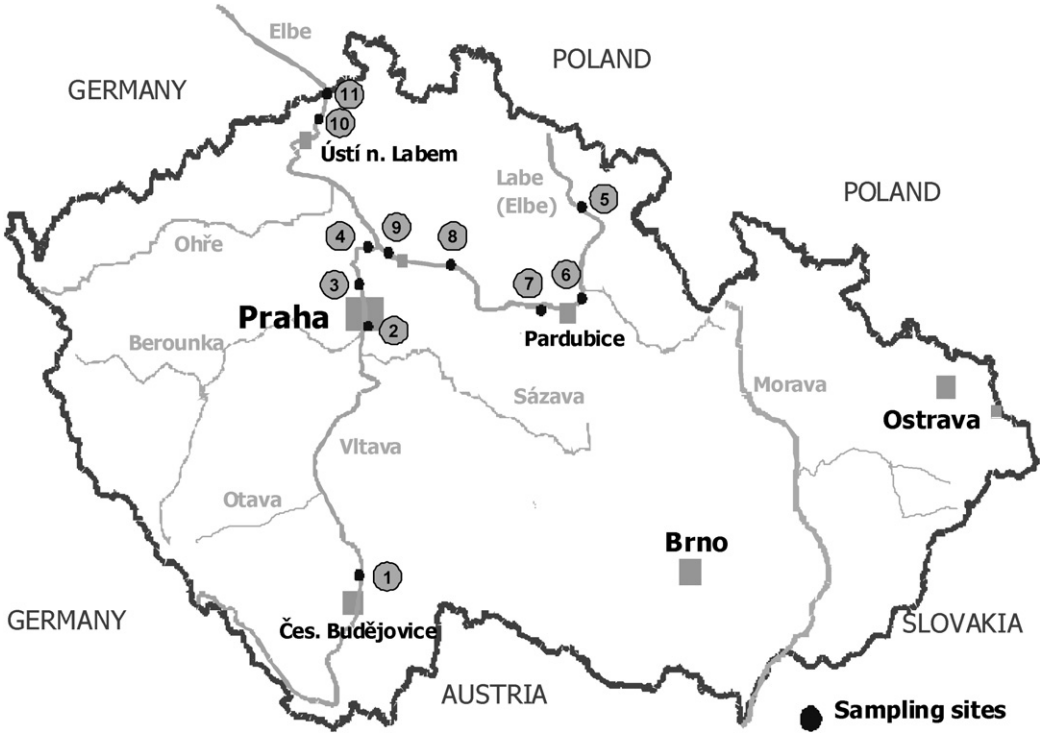

Fig. 1. Sampling localities: (i) Vltava river: (1) Týn nad Vltavou, (2) Podolí, (3) Klecany, (4) Vraňany; (ii) Elbe river: (5) Verdek, (6) Němčice, (7) Valy, (8) Lysá, (9) Obříství, (10) Děčín, (11) Hřensko.

vacuum evaporator (Büchi Rotavapor, France) and the residual solvents were carefully removed by a gentle stream of nitrogen. The samples were dissolved in isooctane containing BDE 37 (0.5 ng ml^{-1}) used as a syringe standard, and treated with concentrated sulphuric acid (approx. three drops) to remove residual lipids.

2.3.3. GC–MS analysis

2.3.3.1. Conventional method employed for BFRs monitoring. An Agilent 6890 (Agilent Technologies, USA) gas chromatograph equipped with electronic pressure control (EPC), a split/splitless injector, a mass selective detector Agilent 5975 XL, and a DB-XLB capillary column (30 m × 0.25 mm i.d. × 0.1 μm film thickness, J & W Scientific, USA) was employed for the analysis of PBDEs and HBCD. The GC conditions were as follows: column temperature program: 105 °C (2 min), 20 °C min^{-1} to 300 °C (5 min); carrier gas: helium with a constant flow of 1.5 ml min^{-1}; injection temperature: 275 °C; injection volume: 1 μl using pulsed splitless injection mode (30 psi); splitless period: 2 min. Mass selective detector with a quadrupole analyser was operated in a negative chemical ionisation (NCI). The ions (*m/z*) selected for monitoring were 79, 81, 159, and 161 (PBDEs) and 326, 328 (PCB 112, internal standard). The ion *m/z* 79 was used for the quantification purposes. Methane used as a reagent gas (purity 99.995%) was set at a pressure of 2×10^{-4} mbar. The ion source and quadrupole temperatures were both 150 °C.

The presence of deca-BDE was monitored using the same GC instrument employing a shorter DB-XLB column (15 m × 0.25 mm i.d. × 0.1 μm film thickness). The GC conditions were as follows: column temperature program: 80 °C (2 min), 20 °C min^{-1} to 280 °C, 5 °C min^{-1} to 320 °C (5 min); carrier gas: helium with a constant flow of 3 ml min^{-1}; injection temperature: 285 °C; injection volume: 1 μl using pulsed splitless injection mode (30 psi); splitless period: 2 min. Monitored ions (*m/z*) were 485 and 487; ion *m/z* 487 was used for quantification.

2.3.3.2. Novel method for BFRs and other halogenated POPs. A GC × GC–TOFMS system Pegasus 4D (LECO, USA) consisted of an Agilent 6890N gas chromatograph equipped with a split/splitless injector, a high-speed time-of-flight mass spectrometer LECO Pegasus III, and an MPS2 autosampler (Gerstel, Germany). Inside the GC oven a dual-stage jet modulator and the secondary oven were mounted. Resistively heated air was used as a medium for hot jets, while cold jets were supplied by gaseous nitrogen, secondary cooled by liquid nitrogen.

A DB-XLB column (30 m × 0.25 mm i.d. × 0.10 μm film thickness, J & W Scientific, USA) was as a first dimension column and a BPX-50 column (1.25 m × 0.1 mm i.d., 0.1 μm film thickness, SGE, USA) as a second dimension column. GC conditions were as follows: injection temperature: 280 °C; interface: 280 °C; first oven temperature program: 90 °C (1.5 min), 10 °C/min to 320 °C (1.0 min); secondary oven temperature program: 110 °C (1.5 min), 10 °C/min to 340 °C (1.0 min); modulation period: 3 s (hot pulse 0.6 s); modulator offset: +35 °C; carrier gas: helium with a constant flow of 1.3 ml min^{-1}; injection

volume: 1 μl pulsed splitless injection mode (50 psi); splitless period: 1.5 min.

The MS detector was operated under following conditions: mass range: *m/z* 50–1000; ion source temperature: 220 °C; detector voltage: −1850 V; acquisition rate: 100 spectra/s.

2.4. Quality assurance/quality control

Using the described methodology, recoveries and detection limits were calculated on the data obtained by validation on spiked fish samples. BFRs recoveries ranged between 86% and 103%, and detection limits were in a range of 0.02–0.2 ng g^{-1} lipid weights. Relative standard deviations (RSDs) of the analytical method (conventional system) were in a range of 3–8%. In addition, procedure blanks were carried out, showing no presence of analytes of interest.

3. Results and discussion

Aggregated data obtained by the analysis of 80 fish samples (three species differing in feeding habits: bream, chub, and perch) obtained in 11 sampling sites in the year 2005 are summarised in Table 1. The occurrence of several PBDE congeners and HBCD (sum of isomers) was documented in all analysed samples. Without any exception, the dominating congener was BDE 47; the levels of this tetra-BDE were about one order of magnitude higher than those of any other monitored congeners (congener BDE 99 in perch was an exception, see Fig. 2a). Relative abundances of PBDE congeners in particular fish species were very similar in all sampling sites; the GC profiles resembled the "pentabromodiphenyl ether" commercial product (typically containing BDE 47 as the major component). This fact was not surprising, because various kinds of these technical mixtures (e.g. Bromkal 70-5DE) were used by the local industry in past decades. Apparently, the same source of pollution was responsible for contamination of aquatic biota collected from other European rivers. Similar results, i.e. major contribution of BDE 47 to the total PBDEs content, were reported (Rahman et al., 2001; de Wit, 2002; Eljarrat et al., 2005; Lacorte et al., 2006; Law et al., 2006; Pulkrabová et al., in press).

As shown in Fig. 2b, an extremely strong correlation ($R^2 = 0.916$) was found between the content of BDE 47 and the sum of all PBDE congeners (data set obtained by analysis all samples considered). From practical point of view, this congener could be easily monitored as a representative indicator of PBDEs group thus enabling simple estimation of the total contamination extent. BDE 47 is commonly well separated on a conventional GC capillary from other detectable components typically present in fish extract hence its identification is not biased. Moreover, due to a relatively high content of BDE 47 in fish, the LOD of this congener is not a limiting factor for the choice of MS detection system. Instead of using an MS detector operated in NCI mode that is needed for detection of trace PBDEs other than BDE 47, common GC–MS employing EI (regardless its lower sensitivity for PBDEs detection) can be used in routine monitoring of this indicator (Čajka et al., 2005).

It should be noted that in spite of a high production rate of BDE 209 and its wide use, which even has increased since the ban of technical penta- and octa-mixtures (www.bsef.com), in none of analysed fish samples the presence of this congener was detected. Until now, only few studies reported at residues of deca-BDE in fish although its levels in sediments were sometimes quite high (Sellström et al., 1998). Contamination of river sediments by BDE 209 was also found in one of our earlier studies concerned with pollution of Czech aquatic ecosystem, i.e. its exposure

Table 1
Levels of PBDE and PCB congeners in fish (μg kg^{-1} wet weight)

	Bream ($n = 15$)				Chub ($n = 45$)				Perch ($n = 20$)			
	Median	Min/Max	Mean	s.d.	Median	Min/Max	Mean	s.d.	Median	Min/Max	Mean	s.d.
Lipids (%)	2.1	0.8/5.0	2.8	1.4	1.8	0.2/6.9	2.1	1.3	1.7	0.4/3.9	1.6	1.1
BDE 28	0.2	0.1/0.5	0.2	0.1	0.1	n.d./1.7	0.2	0.3	0.2	n.d./0.3	0.2	0.1
BDE 47	7.1	2.2/16.1	7.5	3.7	3.5	0.5/27.5	5.3	5.9	2.5	0.4/4.6	2.4	1.5
BDE 49	0.2	0.1/0.3	0.2	0.1	0.1	n.d./0.4	0.1	0.1	0.1	0.1/0.3	0.1	0.1
BDE 66	0.1	n.d./0.1	0.1	0.1	0.1	n.d./0.2	0.1	0.1	0.1	n.d/0.2	0.1	0.1
BDE 85	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	–	n.d.	–
BDE 99	0.1	n.d./0.3	0.1	0.1	0.1	n.d./1.3	0.1	0.2	0.2	0.1/1.9	0.4	0.5
BDE 100	1.0	0.3/2.1	1.0	0.5	0.6	0.1/4.7	0.1	0.9	0.5	0.1/0.8	0.4	0.3
BDE 153	0.2	0.1/0.6	0.2	0.1	0.2	n.d./1.8	0.3	0.3	0.1	n.d./0.2	0.1	0.1
BDE 154	0.4	0.3/0.9	0.5	0.2	0.3	0.1/3.9	0.6	0.7	0.2	n.d./0.3	0.2	0.1
BDE 183	–	n.d.	n.d.	–	0.1	n.d./0.3	0.1	0.1	0.1	n.d./0.1	0.1	–
∑BDEs	9.5	3.2/20.8	9.8	4.7	4.9	0.9/36.0	7.5	8.0	3.9	0.9/6.8	3.8	2.2
HBCD	12.1	0.8/158.0	27.0	45.2	2.1	n.d./14.0	3.3	3.6	2.7	n.d./16.1	3.9	4.6
∑CBs	80.4	29.3/111.1	75.3	28.4	47.8	6.0/354.0	69.6	67.2	35.2	5.4/159.1	43.6	45.3

n.d., not detected; s.d., standard deviation.
∑BDEs = sum of PBDE congeners (28, 47, 49, 66, 85, 99, 100, 153, 154, and 183).
∑CBs = sum of PCB congeners (28, 52, 101, 118, 138, 153, and 180).

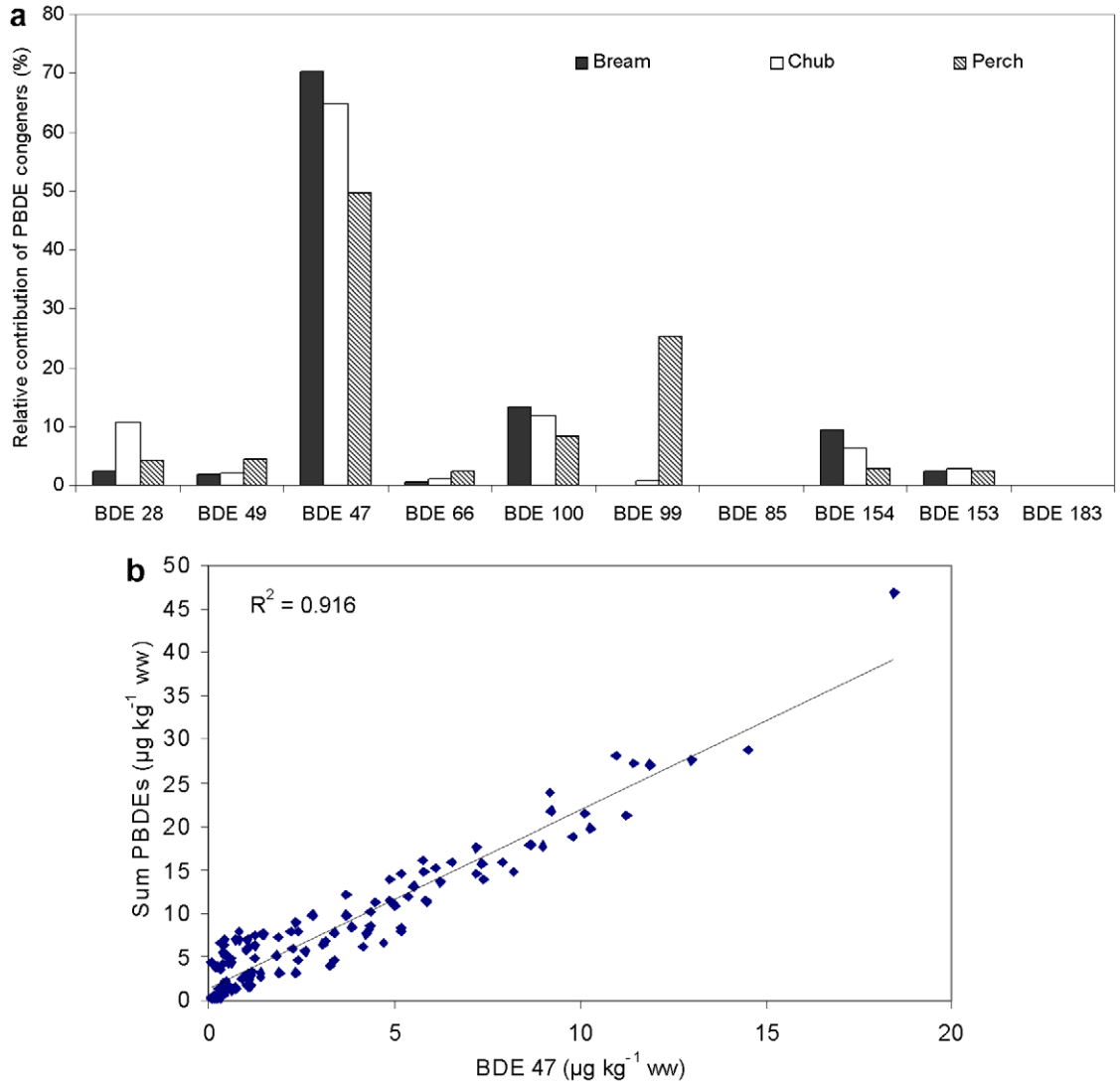

Fig. 2. (a) PBDEs pattern in various fish species collected in locality Hřensko at Elbe River and (b) sum PBDE congeners vs. concentration of BDE 47 (linear regression model). A correlation between two variables indicated by the line.

could theoretically take place (Pulkrabová et al., in press). An unanswered question remains whether this highly lipophilic ($K_{ow} \sim 10$) compound with a large effective volume of its molecule is bioavailable for biota. Alternative explanation of minimal occurrence of deca-BDE congener in aquatic organism is its rapid excretion and/or biotransformation after entering their body (Bezares-Cruz et al., 2004; Eriksson et al., 2004; Eljarrat et al., 2005). In any case, BDE 209 is a relatively labile substance that easily decomposes under environmental conditions in yielding large range of lower brominated PBDEs and also other bromine containing products when illuminated by sunlight (Bezares-Cruz et al., 2004; Eriksson et al., 2004; Söderström et al., 2004). Products of a deca-BDE breakdown may account in this way for unknown bromine signals occurring in GC–MS (NCI), see Fig. 3. It should be noted that due to a very low volatility, deca-BDE cannot be easily analysed together with other PBDE congeners; for its determination the use of a short GC capillary column is preferred. Because of this inconvenience, BDE 209 is not commonly involved in monitoring studies.

Substantial differences of PBDE congeners' pattern were found in perch as compared to other fish species (bream and chub), see Fig. 2a. While in the latter group the contribution of congener BDE 47 to the total PBDEs content was 50–70%, in the predator fish represented by perch significant amounts of congener BDE 99 were found (contribution up to 25% in perch *vs.* 1–4% in chub and bream). Considering relatively low levels of BDE 99 both in omnivorous chub and benthic bream, the relatively high content of this congener was hardly due to differences in dietary exposure. More probably, either other bioaccumulation mechanism or different intensity and/or specificity of metabolic pathways might be responsible for the above mentioned interesting observation.

In Fig. 4, mean values of the major PBDE congener BDE 47 in all biomonitored fish species are shown. Without exception and regardless the mean fat content in fish

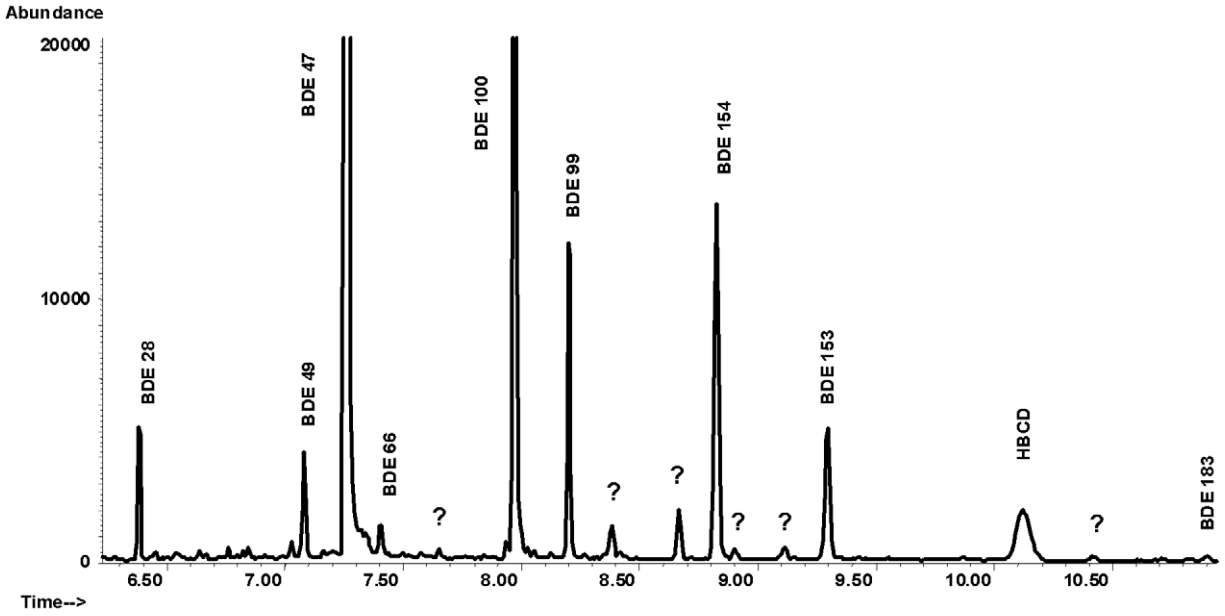

Fig. 3. GC–MS-quadrupole chromatogram (*m/z* 79) of chub extract in NCI mode (locality Klecany on Vltava river). Unknown compounds marked by question marks.

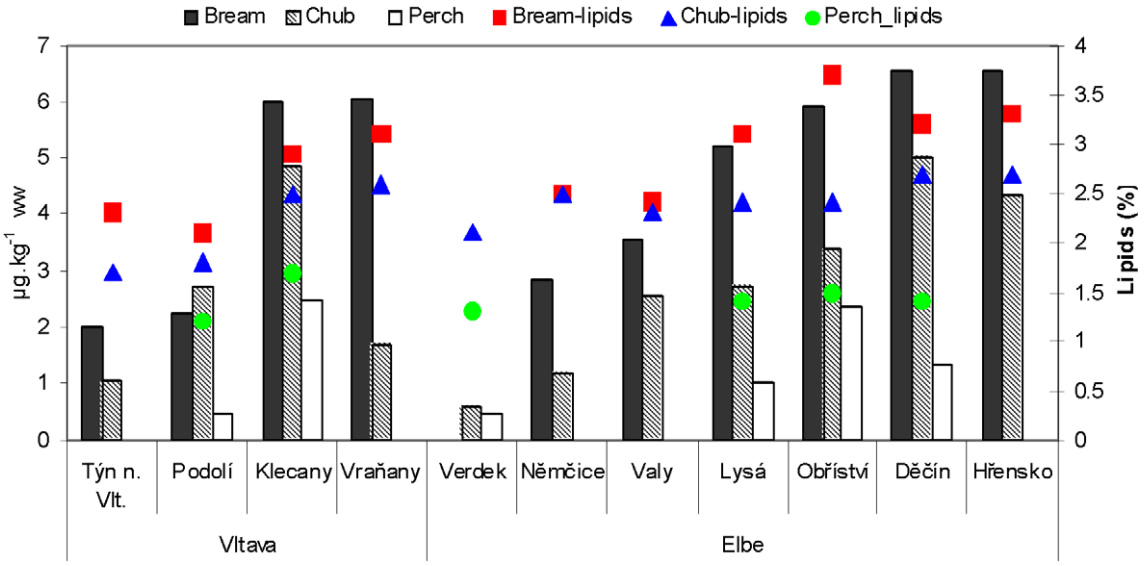

Fig. 4. Congener BDE 47 in three fish species collected in sampling sites located at river Vltava and Elbe.

from particular locality, the bioconcentration potential (expressed in concentration of BFRs in tissues and/or lipids) was in following order: bream > chub > perch. A good correlation ($R^2 = 0.667$) was found between the total PBDE concentrations and lipid content in fish fillets. In Fig. 4, a successive increase of fish contamination downstream alongside both rivers is also documented. Existence of the intensive emission source in Prague industrial area was identified by significant increase of BFR levels in fish from locality Klecany as compared to samples from Podolí.

In Fig. 5, the current fish contamination data are compared with those obtained in our previous study conducted at three localities at river Elbe in the years 2001–2003 (Pulkrabová et al., in press). Although the pollution extent varied among the monitoring years (obviously also because of changes in annual water flows), fish from Valy located downstream from the large industrial city Pardubice were invariably high contaminated. Following the severe floods in the year 2002, locality Hřensko close to the Czech–German border, become more polluted while contamination of fish from locality Valy as compared to other sampling sites rather dropped down. Transport of polluted sediments is assumed to cause of these changes.

Several studies performed in recent 15 years in the European countries were focused mainly on the major PBDE congeners 47, 99, and 100, the source of which are obvi-

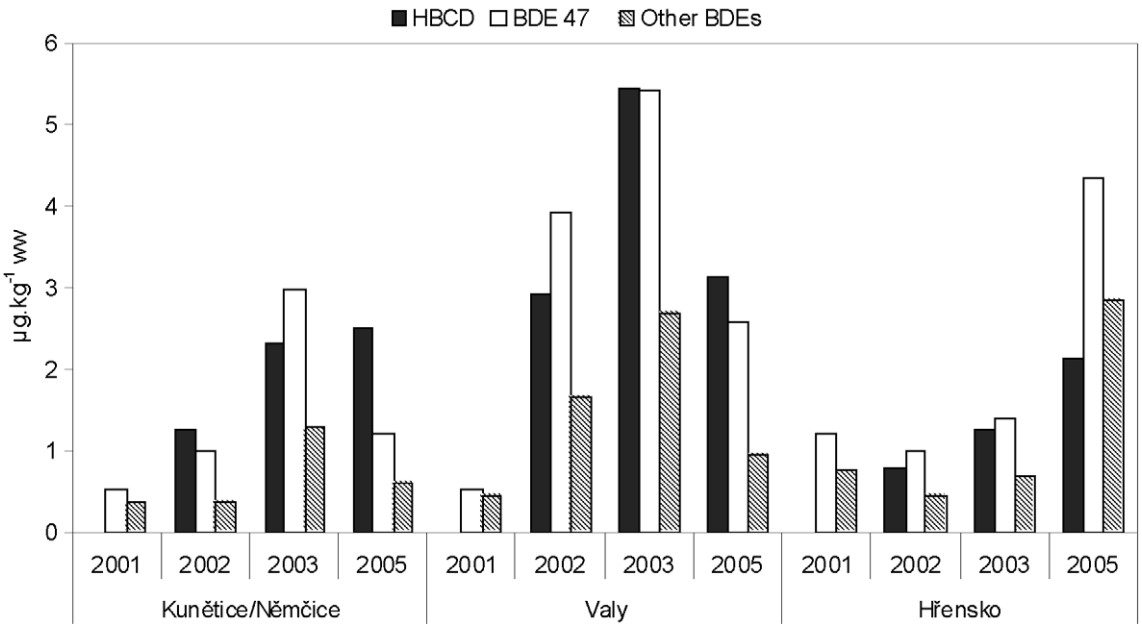

Fig. 5. Time trends in contamination of selected localities at Elbe river. Chub used as a bioindicator.

ously banned penta-mixtures (Allchin et al., 1999; Sellström, 1999; de Boer et al., 2003; Eljarrat et al., 2005). Most of examined fish species were unfortunately different from those involved in our study and therefore, considering varying bioaccumulation potential, the direct comparison of contamination extent is rather difficult. In general, the differences were not too pronounced, the levels of BFRs in bream (one of few "common" fish both involved in this and other studies abroad) collected the most contaminated Czech sampling sites (Klecany, Vraňany, Děčín and/or

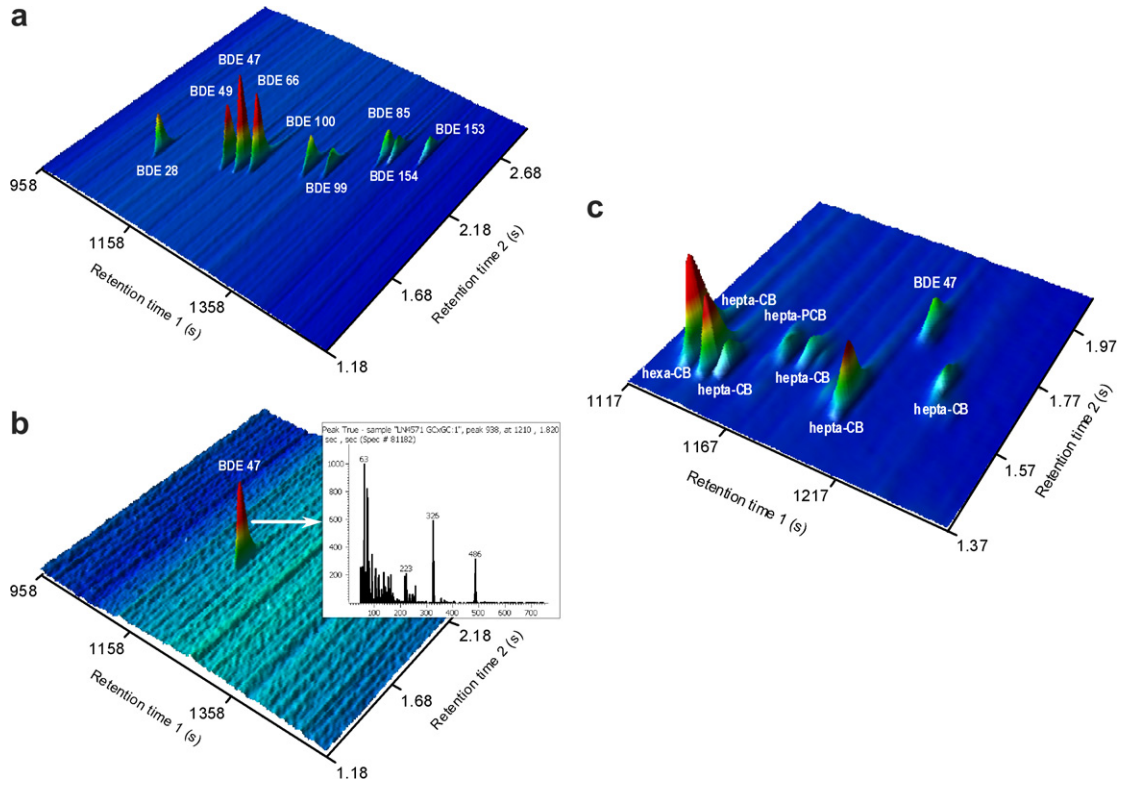

Fig. 6. GC × GC–TOFMS chromatograms of: (a) PBDEs (sum of *m/z* 326, 392, 564, 406, 484, 486, and 562) standard solution in EI mode (300 pg of each analyte injected); (b) BDE 47 (*m/z* 486) in fish extract in EI mode (150 pg injected corresponding to 0.025 mg kg^{-1} wet weight); (c) POPs (hexa-CBs, hepta-CBs, and PBDE 49) contained in fish extract (sum of *m/z* 326, 360, 394, and 486).

Hřensko) were comparable to those found in Dutch or Swedish rivers (Sellström, 1999; de Boer et al., 2003).

In the final phase of this study the potential of comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOFMS) in the analysis of components contained in the sample extract prepared for BFRs analysis was explored. We should note that the sample extraction and purification method employed in BFRs analysis is in principle the same as that one used in the examination of other halogenated POPs, such as PCBs and other chlorinated contaminants. However, regarding the determinative step, MS detector has to be operated in NCI mode whenever high sensitivity needed for analysis of minor PBDE congeners is required (typically levels of which are even by two orders of magnitude lower than most of monitored major chlorinated POPs). Since only abundant, non-specific bromine-containing ions are monitored in analysis of PBDEs/HBCD, information on chlorinated pollutants eluted in similar range of retention times is not recovered.

Thanks to high separation power of GC × GC and availability of full spectral information even at low concentration levels of analytes, significant improvement of analysis efficiency has been obtained by introduction of GC × GC–TOFMS technique. Identification/quantification of major representatives of halogenated POPs and many other components present in the sample extract was possible in a single GC run. In Fig. 6a and b, GC × GC separation of PBDEs standard solution and determination of BDE 47 in fish extract are shown. The unique features of TOFMS enable simultaneous analysis of a wide range of other POPs in fish extract, see Fig. 6c. However, needed to mention, the EI mode (the only available in LECO instrument) did not provide, under conditions set in this study, sufficient LODs for determination the whole range of PBDE congeners present in biotic samples typically at ultratrace levels (although intensive molecular and fragmentation ions – isotopic clusters are present in the high mass region of EI spectra of PBDE congeners). To realise more comprehensive analysis of all trace halogenated POPs, the use of a high-resolution TOFMS operated in NCI mode is a conceivable solution (Čajka et al., 2005; Čajka and Hajšlová, 2007). Further investigations aimed at improvement of performance characteristics of analytical procedures employed in monitoring studies are planned.

4. Conclusions

Two objectives were aimed in this study: (i) collection of new information on the occurrence of BFRs in selected sampling localities at important Czech rivers and (ii) implementation of a novel analytical approach into the monitoring activities concerned with the major groups of POPs. The main conclusions of the study can be summarised as follows:

- Fish is a suitable bioindicator for monitoring of BFRs in aquatic ecosystem; species with higher fat content are preferred because of higher bioaccumulation potential hence possibility to detect even trace components.
- The contamination pattern of fish collected in rivers Elbe and Vltava and its extent are comparable with those reported in other European studies conducted in industrial areas. Technical PBDE mixtures based on penta- congeners were probably the source of pollution.
- The mean contents of both PBDEs and HBCD varied among the monitoring years (current data compared with earlier study), nevertheless fish from the sampling sites located downstream from industrial areas representing a potential emission source were always more contaminated as compared to those upstream from locality.
- GC–MS (NCI) enables sensitive analysis of a wide range of BFRs, however, it does not allow non-target screening. The introduction of GC × GC–TOFMS (EI) provides very comprehensive information on the occurrence of major halogenated POPs contained in sample extract; moreover, other non-target analytes can be identified. On the other hand, the analysis of minor BFRs is impossible due to rather higher LODs as compared to MS operated in NCI mode.

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