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Occurrence of brominated flame retardants and perfluoroalkyl substances in fish from the Czech aquatic ecosystem

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HIGHLIGHTS

- 20 BFRs and 25 PFASs were measured in 48 fish collected in the Czech Republic.
- TBBPA was monitored in the Czech aquatic ecosystem for the first time.
- A content of analytes decreased as follows: PFOS≫PFCAs>PBDEs, HBCDs>FOSA~TBBPA.
- The profiles of HBCD isomers indicated the highest contribution of α-HBCD (88%).

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ABSTRACT

This study reports results of analysis of various groups of halogenated compounds, including brominated flame retardants (BFRs), such as polybrominated diphenylethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and perfluoroalkyl substances (PFASs) in 48 fish samples collected in eight localities from the Czech Republic. In this survey, identification of potential sources of these chemicals was also performed; therefore several sampling sites located in highly industrialized areas were also selected. Perfluorooctanesulfonate (PFOS) was dominating in all tested fish samples. Generally, the content of ∑BFRs was significantly lower, i.e. in the range of 0.21–19.9 μg/kg wet weight, ww (median value 2.37 μg/kg ww) compared to the concentration of ∑PFASs that was in the range of 0.15–877 μg/kg ww (median value 8.5 μg/kg ww). The extremely high content of PFOS (842 μg/kg ww) was found in fish muscle tissue from the locality situated on the Bílina River, where chemical industry is located. This concentration was comparable to those found in similar highly industrialized areas worldwide.

1. Introduction

Environmental contamination by synthetic halogenated xenobiotics such as brominated flame retardants (BFRs) represented by polybrominated diphenylethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA); and perfluoroalkyl substances (PFASs), has become a main concern over the last decade, mainly due to their persistence in the environment and negative influence on living organisms including humans. Several of these contaminants have shown a potential for biomagnification in food chains. Similar to other persistent organic pollutants (POPs), BFR and PFAS groups are subjects of many studies, as they exhibit various adverse effects, including developmental toxicity, immunotoxicity and hepatotoxicity (Labadie and Chevreuil, 2011; Law et al., 2006). In May 2009, several BFRs (penta-BDE and octa-BDE technical mixtures), perfluorooctanesulfonic acid (PFOS) and its salts, together with other halogenated chemicals, were included in the annexes of the Stockholm Convention (2009). With the exception of three commercial PBDEs mixtures, the usage of BFRs has until now mainly comprised of TBBPA and HBCD (EFSA, 2005). As a result of their potential to bioaccumulate in the environment, the goods containing more than 0.1% of penta-BDE and octa-BDE technical mixtures have been prohibited in the EU since August 2004 and the ban was further extended to electrical and electronic goods with deca-BDE in July 2008 (BSEF, 2012; EPCEU, 2003). A global ban of HBCD is currently being considered under the framework of the Stockholm Convention (2013) on POPs and a final decision will be taken in May 2013. The production and use of PFOS is restricted by the directive 2006/122/EC (EPCEU, 2006) and is also under the review for its possible classification as a WFD (Water Framework Directive) Priority Substance or PHS (Priority Hazardous Substance) due to its emission sources (EPCEU, 2008). Regarding perfluorooctanoic acid (PFOA),

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there are voluntary reductions on this hazard chemical; however, it is still manufactured (Clarke and Smith, 2011). The European Union (EU) is currently assessing PFOA and, whilst there are no restrictions at present, a ban could be imposed in the future (Clarke and Smith, 2011). Numerous studies have reported the widespread occurrence of these chemicals in aquatic ecosystem, caused by direct and indirect discharges of both urban and industrial waste, that are associated not only with sediments, but are also transferred in biota (Labadie et al., 2010; Pulkrabová et al., 2007). In the past decades, the list of halogenated POPs targeted in various monitoring surveys has largely expanded (Furdui et al., 2007; Labadie and Chevreuil, 2011; Macgregor et al., 2010; van Leeuwen and de Boer, 2008; van Leeuwen et al., 2009; Zhao et al., 2011). These studies documented a variability of reported levels for these two groups of halogenated contaminants (sum or for individual compounds) with concentrations ranging mostly from 0.01 μg/kg to 200 μg/kg wet weight (ww). Also the dependence of determined concentrations on fish species and potential sources of contamination was observed. Bioindicators like fish represent a useful tool for the monitoring of their presence and concentrations (Hajšlová et al., 2007). The number of organochlorinated and other "classic" POPs, such as PBDEs and HBCDs have been investigated in several environmental surveys conducted in the Czech Republic during the last decade (Hajšlová et al., 2007; Hrádková et al., 2012; Pulkrabová et al., 2007; Randák et al., 2006; Svobodová et al., 2003; Vávrová et al., 2003). On the other hand, no large-scale study focusing on the determination of PFASs and TBBPA in fish samples has been performed in the Czech Republic until now.

The presented study was focused on the monitoring of pollution of selected Czech rivers and streams by BFRs and PFASs. Altogether 48 fish samples collected at different places in the Czech Republic were examined. The main objectives of this survey were: (1) to determine the extent of aquatic ecosystem pollution by selected halogenated (brominated and fluorinated) compounds by the analysis of fish collected in various rivers of the Czech Republic and (2) to compare our results with similar studies conducted in the Europe, Nord America and Asia.

2. Material and methods

2.1. Chemicals and reagents

Certified standards of 23 BFRs including internal standards (BDE 28, 37, 47, 49, 66, 77, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209, ^{13}C-BDE 209; α-, β-, γ-HBCD; α-$^{13}C_{12}$ HBCD and TBBPA) and 39 PFASs including 25 native standards (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA, PFBS, PFHxS, PFOS, PFDS, PFHxPA, PFOPA, PFDPA, FOSA, N-EtFOSA, N-EtFOSE, N-MeFOSA, N-MeFOSE) and 14 isotopically labeled internal standards ($^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_8$-PFOA, $^{13}C_9$-PFNA, $^{13}C_6$-PFDA, $^{13}C_7$-PFUnA, $^{13}C_2$-PFDoA, $^{18}O_2$-PFHxS, $^{13}C_8$-PFOS, $^{13}C_8$-FOSA, d_5-N-EtFOSA, d_9-N-EtFOSE, d_7-MeFOSE, Cl-PFHxPA) used within this monitoring study were provided by Wellington Laboratories (Guelph, Ontario, Canada); see supplementary materials (Table S1). Working standard solutions of 16 PBDEs in isooctane (concentration in calibration solutions ranged from 0.05 to 100 ng/ml) and standard solutions of 3 HBCD isomers, TBBPA and 25 PFASs in methanol (concentration in calibration solution ranged from 0.05 to 10 ng/ml) were stored at 5 °C. Organic solvents — hexane, cyclohexane, isooctane, ethyl acetate, dichloromethane and methanol were supplied by Merck (Darmstadt, Germany) and acetonitrile by Sigma-Aldrich (Seelze, Germany). All solvents were of "organic trace analysis" grade. Anhydrous sodium sulfate and sodium chloride were from Penta (Chrudim, Czech Republic). Bio Beads S-X3 (styrene–divinylbenzene gel, 200–400 mesh) was purchased from Bio Rad Laboratories (Benicia, CA, USA). Sulfuric acid (98%) was obtained from Merck. Anhydrous magnesium sulfate, activated charcoal (untreated powder, 100–400 mesh), ammonium acetate (99.99%), formic acid (95%), Supelclean ENVI-Carb (particle size: 120–400 mesh) were supplied by Sigma Aldrich. Bondesil C18 sorbent (40 μm) was from Varian (CA, USA).

2.2. Samples collection

Altogether 48 fish samples including 27 common breams (*Abramis brama*), eight European chubs (*Squalius cephalus*), six roaches (*Rutilus rutilus*), a crucian carp (*Carassius carassius*), a European perch (*Perca fluviatilis*), a gudgeon (*Gobio gobio*), a grayling (*Thymallus thymallus*), a common carp (*Cyprinus carpio*), a rainbow trout (*Oncorhynchus mykiss*) and a rudd (*Scardinius erythrophthalmus*) were caught during the period from August to October 2010. The main characteristics of fish samples examined within this study are summarized in Table 1. Fish samples were collected at 15 different sampling localities on the following Czech rivers: Labe, Vltava, Bílina, Lužická Nisa, Morava and Dyje; see Fig. 1. The Vltava River is the longest river in the Czech Republic going through the capital of the Czech Republic and several industrial localities and finally flows into the Labe River. The Labe River is one of the most important European rivers along which many important chemical factories and other branches of industry (i.e., paper-mill) are situated. The other sampling site is on the Bílina River, which is a tributary of the Labe River, and is classified as highly polluted river in the Czech Republic (Hajšlová et al., 2007; Hrádková et al., 2012). This locality was downstream from a large chemical factory in the Czech Republic that manufactures e.g. hydrofluoric acid (HF), sodium fluoride (NaF), chlorine, hydrochloric acid etc. The Lužická Nisa River is a river in the northern part of the Czech Republic, which forms the boundary between the Czech Republic and Poland, going through the locality with textile industry and then flowing into the Odra River. The Dyje River, which is a tributary of the Morava River, is going through the southern part of Moravia near the border with Austria, and through the National Park Podyjí. On the Dyje River there are no chemical factories or other branches of industry. The Morava River is the most important river in the southern part of Moravia forming the boundary between the Czech Republic and Slovakia going through the locality with food and textile industry and flowing into the Danube River in Slovakia. The fish samples were shipped to the laboratory as whole frozen fish and stored in freezer at approx. −20 °C. Their body length ranged from 12 to 40 cm, body circumference from 14 to 49 cm and age from one to ten years. Before the homogenization, the skin was removed and fish was filleted.

2.3. Sample preparation, extraction and clean-up

2.3.1. PBDEs

The analytical procedure used for the analysis of PBDEs in fish tissue samples was described in detail in the earlier study (Hajšlová et al., 2007). Briefly, approximately 20 g of fish muscle tissue were homogenized with anhydrous sodium sulfate (50 g). The samples were extracted in a Soxhlet apparatus for 8 h using 170 ml of hexane:dichloromethane mixture (1:1, *v*/*v*). After the solvent evaporation, the residues were weighted for the lipid determination. An aliquot of isolated fat (ca. 750 mg) was dissolved in 10 ml of cyclohexane:ethylacetate solution (1:1, *v*/*v*) and then purified using gel permeation chromatography (GPC) on a column filled with Bio Beads S-X3 stationary phase and cyclohexane:ethyl acetate (1:1, *v*/*v*) used as a mobile phase. A fraction corresponding to an elution volume of 14–30 ml was collected. This fraction was after evaporation re-dissolved in 0.5 ml isooctane with syringe standards (BDE 37 and BDE 77 5 ng/ml, $^{13}C_{12}$-BDE 209 50 ng/ml) and treated with concentrated sulfuric acid (approx. three drops) to remove residual lipids.

2.3.2. HBCDs and TBBPA

HBCDs and TBBPA were isolated from the sample using a modified method described by Lacina et al. (2011). The procedure was based on the extraction with acetonitrile followed by purification using