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Emerging brominated flame retardants and dechlorane-related compounds in European eels (*Anguilla anguilla*) from Latvian lakes

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HIGHLIGHTS

- Occurrence of EBFRs and DRCs in eel samples from Latvian lakes was evaluated.
- Among the EBFRs, HBCD and DBDPE were found in eels in quantifiable concentrations.
- Dec 602 was the predominant component among selected DRCs.
- The increase of POP concentrations with fish age was observed for HBCD and DRCs.
- Levels of selected contaminants in eels from Latvia are lower than in other regions.

GRAPHICAL ABSTRACT

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ABSTRACT

Fifteen halogenated flame retardants (HFRs) including seven emerging brominated flame retardants (EBFRs) and eight dechlorane-related compounds (DRCs) were analyzed in eels (*Anguilla anguilla*) sampled from five Latvian lakes. Out of the seven EBFRs, hexabromocyclododecane (HBCD) and decabromodiphenyl ethane (DBDPE) were found in eels in quantifiable concentrations, up to 6.58 and 33.0 ng g^{-1} lipid weight (l.w.), respectively. The mean total concentration of DRCs ($\sum_{DRC}$) in the samples was 0.62 ng g^{-1} l.w. and the geographical distribution of DRC contamination was nearly uniform among the selected lakes. Dechlorane 602 (Dec 602) was the predominant component, whereas the composition of mixture containing *syn-* and *anti*-Dechlorane Plus (DP) stereoisomers showed a pronounced enrichment of the *anti*-DP isomer and was close to the composition of OxyChem® DP commercial product. The determined concentrations of HFRs were lower than in other studies of aquatic biota from Europe and Asia, and the obtained results reflect the acceptable environmental status of Latvian lakes with regard to the total content of HBCD ($\sum_{HBCD}$), considering the environmental quality standards (EQS) stated in the Directive 2013/39/EU. The highest $\sum_{HBCD}$ levels were observed in eels from lakes corresponding to the industrialization of those areas, while the results of principal component analysis (PCA) showed that the concentration of HBCD depended on the particular sampling lake, reflecting non-uniform contamination of the Latvian environment with this EBFR.

1. Introduction

Persistent organic pollutants (POPs) are of global concern because of their toxicity, bioaccumulation, and the potential for

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long-range transport. Due to the bioaccumulation in food webs, POPs pose significant risks to the environment and human health (WHO/UNEP, 2013). Considering the behavior and fate of POPs, marine and freshwater environments are highly affected by these compounds and the contamination status of aquatic environments could reflect the overall extent of pollution in the surrounding area (Wenning and Martello, 2014). While the high degree of pollution with POPs in the Baltic Sea environment has been known for several decades (Helkom, 2004; Koistinen et al., 2008), there is a notable knowledge gap on POP levels in the inland aquatic environments of the Baltic region. Only few references report the levels of such POPs as polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls (PCDD/Fs and PCBs), as well as polybrominated diphenyl ethers (PBDEs) in freshwater fish from the Baltic countries (Zacs et al., 2013, 2016). Considerable political and scientific interest over the past decades has been attracted by halogenated flame retardants (HFRs), with a special emphasis on emerging brominated flame retardants (EBFRs) (Iqbal et al., 2017). These compounds are used on a large scale in order to lower the flammability of materials used in electronic devices, plastics, polystyrene foams, textiles, paints, and other consumer materials (D'Silva et al., 2004). After restrictions imposed on the applications of PBDEs due to their adverse effects to the environment and human health (European Court of Justice, 2008) there has been a growing demand for alternate flame retardants, and therefore the usage of EBFRs has significantly increased. Nevertheless, these alternative BFRs also showed POP-like properties similar to those of PBDEs. The use and disposal of articles containing EBFRs resulted in their presence in various environmental samples, as confirmed by recent studies (Iqbal et al., 2017). Among the EBFRs, hexabromocyclododecane (HBCD) is one of the most widely used FRs in Europe (Covaci et al., 2006). However, due to its toxicity and the specific POP properties, legal and administrative measures were recently requested by the European Commission with regards to the production, use, import and export of this compound (Commission Regulation (EU) No 2016/293). A number of brominated chemicals have been recognized as EBFRs (e.g., 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE)), although very scarce data is available about the occurrence of the majority of these compounds, and in order to implement effective strategies for the minimization of possible hazardous effects of these compounds, such information was requested by the relevant authorities (Commission Recommendation (EU) 2014/118/EU; EFSA, 2012). Other promising contenders expected to fill the vacant niche in the market of FRs after the prohibition of PBDEs were norbornene-based FRs, among which the most important representatives are Dechlorane Plus (DP), which is classified by the United States Environmental Protection Agency (US EPA) as a high production volume chemical (Ren et al., 2008), Dechlorane 602 (Dec 602), Dec 603, and Dec 604 (Shen et al., 2011a,b). However, compounds belonging to the family of dechlorane-related compounds (DRCs) were later found to be toxic and exhibiting the properties of POPs (Chen et al., 2017). Moreover, recent studies reflect a notable increase of DRC levels in the environment, therefore attracting the attention of scientists in the field of environmental protection. (Li et al., 2014; Liu et al., 2016).

Aquatic biota serves the role of a versatile indicator that can accumulate POPs and thus reflect the overall contamination status of the environment. The European eel (*Anguilla anguilla*) is a carnivorous, catadromous fish, which is widely distributed throughout Europe. Eel absorbs and concentrates the bioaccumulative organic pollutants that are present in low concentrations in its diet consisting of crustaceans, worms, snails, larvae, and small fish. For these reasons, eels have long been considered as a bioindicator species that can point to the contaminants present in local habitats (Malarvannan et al., 2014; Roosens et al., 2010; Santillo et al., 2005). The occurrence of FRs in eels has been documented in a number of publications (Bragigand et al., 2006; Malarvannan et al., 2014; McHugh et al., 2010; Roosens et al., 2010; Suhring et al., 2013, 2014, 2015; Ten Dam et al., 2012; Zacs et al., 2016). While the levels of legacy BFRs like PBDEs in eels from Latvian lakes have been recently reported (Zacs et al., 2016), there are no data on the occurrence of EBFRs and DRCs in inland aquatic biota in Latvia. Such information is of great importance for the assessment of contamination status of the Latvian environment, complementing the characterization of the overall situation regarding POPs in European environment and providing an insight into the bioaccumulation and persistence trends of these relatively new compounds in such bioindicator species as the European eel. Therefore, this study aims to investigate the concentration of EBFRs and DRCs in eels sourced from five Latvian freshwater lakes selected to representatively cover the geography of the region and to compare these results to the levels of the same pollutants in eels from other European countries.

2. Materials and methods

2.1. Sample collection and storage

Fifty eight eel (*Anguilla anguilla*) specimens of various length and weight were caught in Latvian freshwater lakes during the period from September 2013 to May 2014 at the 5 locations shown in Fig. 1. These locations were carefully selected to evenly cover all essential eel stocks in the Latvian territory and also to have a maximum variation in body weight and length. At least five eel specimens were collected to represent each sampling site. The samples were packed in polyethylene bags, uniquely coded, and stored with ice during delivery to the laboratory. The average length and weight of eels were 76 cm (ranging from 39 to 101 cm) and 1.0 kg (ranging from 0.10 to 1.87 kg). The age of eel specimens was determined at the National Marine Fisheries Research Institute (Gdynia, Poland) by applying otolith image analysis. The age was established only for 60% of the collected specimens and was found to be in the range from 11 to 30 years. The lipid content of samples was determined within the scope of a previous study (Zacs et al., 2016) and it was in the range from 20 to 41%. The specimens were dissected, musculature (including subcutaneous fat) was isolated and homogenized using a food blender (Kenwood FP101T, Kenwood Ltd, UK), and the homogenates were packed into polyethylene bags and stored at −18 °C until analysis.

2.2. Chemicals and materials

Standard solutions of individual $^{13}C_{12}$-labeled α-, β-, and γ-HBCD diastereomers, native Dec 602, *syn*-DP, *anti*-DP, and their isotopically labeled surrogates $^{13}C_{10}$-Dec 602, $^{13}C_{10}$-*syn*-DP, $^{13}C_{10}$-*anti*-DP, as well as $^{13}C_{12}$-PCB-194 were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Certified standards of target FRs, namely, α-HBCD, β-HBCD, γ-HBCD, (2,3-dibromopropyl) (2,4,6-tribromophenyl) ether (TBP-DBPE), hexabromobenzene (HBB), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexachlorocyclopentadienyldibromocyclooctane (DBHCTD) and tetradecabromo-1,4-diphenoxybenzene (TDBDPB) were supplied by AccuStandard, Inc. (New Haven, CT, USA). The DP derivatives decachloropentacyclooctadecadiene (Cl10DP) and undecachloropentacyclooctadecadiene (Cl11DP) were supplied by Wellington Laboratories (Guelph, ON, Canada), while Mirex, Dec 603, and Dec 604 were obtained from Santa Cruz Biotechnology (Dallas, TX, USA). Stock solutions were prepared in toluene or in