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Spatial variations in the levels and isomeric patterns of PBDEs and HBCDs in the European eel in Flanders

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ABSTRACT

Pooled yellow eel (*Anguilla anguilla* L.) samples, consisting of 3–10 eels, from 50 locations collected in the period 2000–2006 were used to assess the pollution with PBDEs and HBCDs in Flemish waters (Belgium). Results from this monitoring network are presented and the spatial aspect throughout Flanders is included, linking POP levels to the industrial characteristics of the different sampling locations. The following PBDE congeners were measured using GC/MS: 28, 47, 49, 66, 85, 99, 100, 153, 154, 183 and 209. Concentrations of ∑PBDE ranged between 10 and 5811 ng/g lipid weight (lw) with a median value of 81 ng/g lw. BDE 47 dominated the PBDE profile in the majority of the eel samples, except for six samples, in which BDE 209 was the dominating congener. These latter samples are probably associated with recent exposure to the Deca-BDE mixture. Three HBCD diastereoisomers (α-, β- and γ-HBCD) were measured using LC/MS-MS. ∑HBCDs ranged between 16 and 4397 ng/g lw, with a median value of 73 ng/g lw. α-HBCD was the dominant isomer in all eel samples. Sediment concentrations of PBDEs were available from four locations and were used to compare the PBDE profile with those in eel. An important shift in the profile was observed, especially for BDE 209. While BDE 209 was only found in 12 eel samples, it was the dominant congener in all sediment samples. This could be due to its metabolisation or degradation in biota combined with the poor uptake of BDE 209 from sediments and its very low water solubility. No HBCDs were detected in any of the sediment samples. No significant correlation could be found between concentrations of PBDEs in eel and sediment from the same location. Comparison with previous studies shows that PBDE and HBCD levels in Flemish eels have decreased rapidly between 2000 and 2006 at particular sites, but alarming concentrations can still be found at industrialized hot spots. This finding is reflected in the human exposure to PBDEs and HBCDs through eel consumption. For average consumers (2.9 geel/day), intakes ranged between 3 and 2295 ng/day for ∑PBDEs (with a median value of 16 ng/day) and between 3 and 1110 ng/day for ∑HBCDs (with a median value of 18 ng/day), respectively. Additionally, human intakes were calculated for recreational fishermen, eating up to 12 g or 86 geel/day. Intakes of those risk groups were higher in comparison with average consumers and were above reference doses described in literature which may induce adverse effects.

1. Introduction

Brominated flame retardants (BFRs) have been extensively used in consumer products such as plastics, textiles, furnishing foam, and electronic circuit boards (Rahman et al., 2001) to reduce the risk of fire and meet fire safety regulations (Alaee et al., 2003). Once released from these consumer products (during production, recycling procedures or usage) BFRs tend to be stable and persist in both terrestrial and aquatic environments. Additive BFRs, such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), are more easily released into the environment compared to their reactive counterparts because they are not chemically bound to the matrix. Due to their toxic effects, including endocrine disruption at the level of the thyroid gland and reproduction system, the usage of Penta- and Octa-BDE mixtures has been banned in Europe since August 2004 (Directory 2003/11/EC). Evidence of environmental debromination of BDE 209 leads to its restricted use in July 2008 by the European court of justice (Betts, 2008). HBCD usage is currently still allowed although risk analysis showed HBCD fulfils all Persistent, Bio-accumulative and Toxic (PBT) criteria and is included in the PBT list of the European chemical substance information system (ESIS). Despite these efforts, high environmental levels have recently been found near sites of human activity (Roosens et al., 2008) which demonstrates the importance of ongoing monitoring studies.

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The aims of the present study were to investigate current PBDE and HBCD distribution in eels throughout a bio-monitoring network in the freshwater system in Flanders and to compare the isomeric profiles of PBDEs and HBCDs in eels and sediments from the most polluted areas. As fish is an important part of human diet, human exposure through intake of Flemish eel was assessed for both the normal Flemish population and for risk groups such as recreational fishermen. European eel (*Anguilla anguilla* L.) in its yellow eel stage was chosen as bio-indicator for the monitoring of environmental contaminants as this stage is characterised by primarily sedentary behaviour (Belpaire and Goemans, 2007). Eel analysis gives a representative description of contamination patterns surrounding the area where it was caught. Furthermore, eel is a fatty fish species, assuring an optimal accumulation of lipophilic contaminants, such as BFRs (Belpaire, 2008). The current study expands the knowledge regarding PBDE and HBCD concentrations, their patterns, distribution profiles and time trends in the freshwater system in Flanders.

2. Materials and methods

2.1. Samples

Yellow eels were collected between 2000 and 2006, from 50 various locations throughout Flanders (Belgium) by the Flemish Research Institute for Nature and Forest (INBO) (Fig. 1). Locations are situated in the catchments of the rivers Ijzer, Scheldt and Meuse and were characterised as rivers or brooks, canals, polder water courses or closed water bodies such as old meanders, ponds or lakes (Table 1). Fish were collected using fyke nets or electro-fishing techniques. Between 3 and 10 eels were caught per location, an amount ranging between 1 and 4 g of their muscle tissue was pooled and analysed for PBDE congeners (28, 47, 49, 66, 99, 100, 154, 153, 183 and 209) and HBCD (α-, β- and γ-) isomers. Detailed information on the number of eels per pooled sample, the size range, weight range, lipid range and sex are given in Table 1.

2.2. Analytical methods

PBDEs reference standards were bought from Wellington Laboratories (Guelph, ON, Canada) and Accustandard (New Haven, CT, USA). Standards of individual ^{12}C-HBCD and ^{13}C-HBCD isomers were purchased from Wellington Laboratories. All solvents used for the analysis (acetone, dichloromethane, *iso*-octane, *n*-hexane, and methanol) were of SupraSolv® grade (Merck, Darmstadt, Germany). Sodium sulphate (Merck) and silica gel (0.063–0.200 mm, Merck) were prewashed with *n*-hexane and heated overnight at 150 °C before use. Extraction thimbles (25 × 100 mm, Whatman®, England) were pre-extracted for 1 h with hexane/acetone (3/1; *v*/*v*) and dried at 100 °C for 1 h. Empty polypropylene columns for clean-up (25 mL) were purchased from Alltech (Lokeren, Belgium).

About 1 g pooled eel muscle sample was weighed, homogenised with Na_2SO_4 and spiked with internal standards (BDE 77, BDE 128, ^{13}C-BDE 209, ^{13}C-α-HBCD,^{13}C-β-HBCD and ^{13}C-γ-HBCD), hot Soxhlet extracted during 2 h with hexane:acetone (3:1) and cleaned-up on acidified silica (Voorspoels et al., 2003). Prior to the clean-up, a fraction of the extract was taken to determine the lipid content gravimetrically. Minor adaptations were required as PBDEs were analysed with GC–ECNI/MS and HBCDs with LC–MS/MS. The cleaned extract was evaporated to dryness, redissolved in 0.5 mL hexane and eluted from pre-packed silica cartridges (Varian) with 6 mL hexane (for GC analysis) and 6 mL DCM (for LC analysis). Both fractions were evaporated to incipient dryness and redissolved in 100 μL *iso*-octane and 100 μL methanol, respectively.

The determination of PBDEs was performed with an Agilent 6890GC-5973MS equipped with a 15 m × 0.25 mm × 0.10 μm DB-5 capillary column and operated in electron capture negative ionisation (ECNI) mode. The ion source, quadrupole and interface temperatures were 250, 150 and 300 °C, respectively. Helium was used as carrier gas at constant flow (1.0 mL/min) and with methane as moderating gas. The MS was operated in SIM mode (*m*/*z* 79 and 81 were monitored for the entire run, *m*/*z* 487 and 495 were monitored for BDE 209 and ^{13}C-BDE 209, respectively). Dwell times were set to 40 ms. One μl of

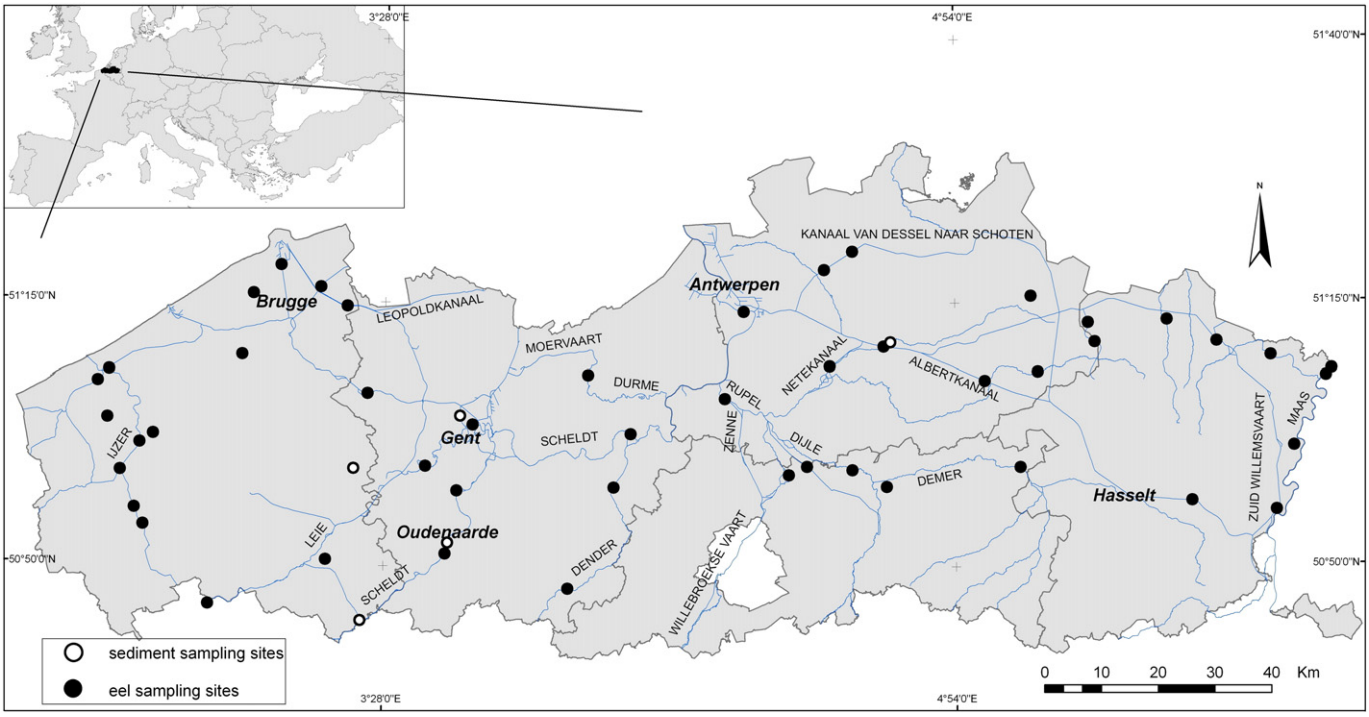

Fig. 1. Locations used for eel and sediment samplings.