

BROMINATED FLAME RETARDANTS IN EEL FROM THE SCHELDT RIVER (BELGIUM)

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Abstract

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), were measured in pooled eel samples originating from different locations along the river Scheldt, including 2 reference locations (closed water bodies), all situated nearby Oudenaarde. Total HBCD levels (range 70 – 10 100 ng/ lipid weight) in the eel samples were measured by GC-MS and were higher than PBDE levels (40 – 1 010 ng/g lipid weight), probably related to the textile industries nearby Oudenaarde. The predominant PBDE congeners were BDE 47, 100, 99 and 49, originating from the former use of the Penta-BDE formulation. The high variation in contamination levels between the different sampling locations resulted in a variable contribution to the total human exposure through eel consumption, ranging between 3 ng and 327 ng/day for PBDEs for normal eel consumers. Decreasing contamination levels of PBDEs and HBCD over the period of 6 years were observed in eel for the same locations. However, these levels are still an order of magnitude higher than levels reported in other studies in Flanders.

Introduction

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) have become the subject of intense research because of possible adverse health effects acknowledged for these compounds¹. PBDEs are chemically and structurally similar to PCBs but are still produced and used in great amounts. All of the summarized organochlorine contaminants can reach the environment through leaching during production and application processes, through volatilization and leaching during use and through particulate losses during use and disposal². Industrial point sources of production or use of these compounds often lead to contamination of nearby aquatic systems, directly leading to increased levels in aquatic organisms such as fish. Besides, the aquatic environment seems to effectively concentrate and biomagnify BFRs³.

The present study aims to evaluate the occurrence of PBDEs and HBCD in pooled eel samples collected from different locations of the Scheldt basin situated near point contamination sources. Previous studies conducted on the same locations have found extreme high levels of PBDEs and HBCD in eel⁴. Additionally, the contribution of strongly contaminated eel versus eel from cleaner areas to the total human dietary exposure was assessed. Although other fish species were also collected and analysed, we present here only results for the eel samples.

Materials and Methods

Eel (*Anguilla anguilla*) was collected in 2006 from 7 different locations in the Scheldt basin. Figure 1 shows the Scheldt basin and locates the area of sampling, namely Oudenaarde (west of Brussels). This area is known for its intensive textile industry, resulting in severe pollution of the nearby aquatic environment. Two closed water bodies, L1 and L2, were included as reference areas, whereas locations L3 to L7 are situated on the river Scheldt and numbered from upstream (L3) to downstream (L7) of Oudenaarde.

Samples were pooled per location and consisted in a variable number between 1 and 10 individuals, resulting in 10 (pooled) samples. Eel could not be caught at location L3. Each sample was analyzed for PBDE congeners 28, 49, 47, 66, 100, 99, 154, 153 and 183, together with total HBCD. The method used for the sample extraction and clean-up has been previously described and validated and was used with minor modifications⁵.

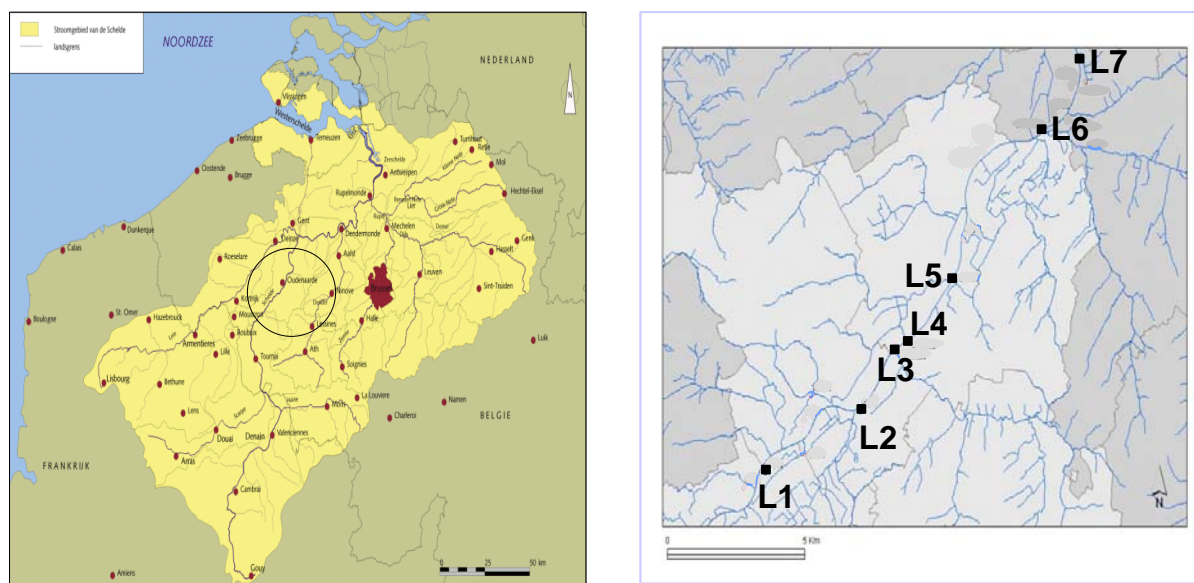


Figure 1. Basin of the river Scheldt and sampling area showing the different sampling locations (L1 to L7).

A homogenised sample of ~1.5 g fish tissue was weighed, mixed with anhydrous Na_2SO_4 and spiked with internal standards (BDE 77 and 128). The extraction was carried out with 100 ml hexane/acetone (3:1, v/v) for 2 h in an automated hot Soxhlet. The lipid content was determined gravimetrically on an aliquot of the extract, while the rest of the extract was cleaned up on ~8 g acidified silica and PBDEs and HBCD were eluted with 15 ml hexane and 10 ml dichloromethane. The eluate was concentrated to 100 μl under a gentle nitrogen stream and transferred to an injection vial.

The determination of PBDEs and HBCD was performed with an Agilent 6890GC-5973MS equipped with a 15 m x 0.25 mm x 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 and the electron multiplier voltage was set at 2100 V. One μl of the extract was injected in solvent vent mode and the splitless time was 1.50 min. The temperature of the DB-5 column was programmed from 90°C, kept for 1.5 min, then increased with 15°C/min to 295°C, kept for 15 min. Dwell times were set to 40 ms. Ions m/z 79 and 81 were monitored for the entire run.

The analytical procedures were validated through analysis of procedural blanks, duplicate samples, and certified material SRM 1945 (Organic pollutants in whale blubber) which has also indicative values for PBDEs. Obtained values were not deviating with more than 10% from the certified values. The quality control scheme is also assessed through regular participation to interlaboratory comparison exercises organized by AMAP and NIST. For each analyte, the mean procedural blank value was used for subtraction. The method LOQs were calculated as 3 x SD of the procedural blanks, taking into account the amount of sample for analysis (~2 g). LOQs for PBDEs range between 2 - 4 ng/g lipid weight (lw) and 5 ng/g lw for total HBCD. Samples with concentrations below LOQ were calculated as $f \cdot \text{LOQ}$ with f being the fraction of samples above LOQ.

Results and Discussion

Geographical variation

Contamination levels are discussed per sampling location. Average values of the sum PBDEs and HBCD were calculated and plotted for each location. The sum PBDEs (BDE 28, 47, 49, 66, 99, 100, 153, 154, and 183) in the analysed eel samples ranged between 40 and 1 010 ng/g lw, while total HBCD values covered a larger range of concentrations (70 – 10 100 ng/ lw) and were generally higher than PBDEs. PBDEs could be measured in every sample (Figure 2). Locations 1 and 2 were included in this study to test for a possible atmospheric contribution in the contamination of the aquatic environment. Our results show that there are high contamination levels along the river Scheldt (L3 through L7), but not in the closed water bodies in the close vicinity (L1 and

L2). Atmospheric contribution to BFR contamination in waters looks to be far less than the contamination directly through the water. Hence, these locations (L1 and L2) can be seen as reference locations for this study.

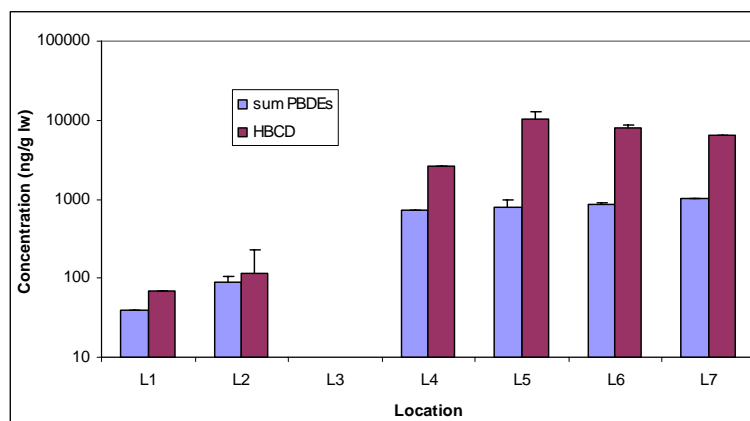


Figure 2. Geographical distribution of average sum of PBDEs and HBCD levels in eel samples along the sampling locations. Error bars represent standard deviations.

It is known that a high density of textile industry can be found upstream Antwerp. A substantial number of these industries use BFRs in their products. The processes by which BFRs are impregnated in the end-products could lead to losses into the aquatic environment. This is supported by the contamination patterns seen at locations L4 to L7, dominated by HBCD. It should be emphasised that even distant locations (L6 and L7) situated downstream Oudenaarde presented high levels of HBCD. This underlines the impact of industrialised areas on the aquatic system, both at local and regional scale.

The following PBDE congeners contributed most to the sum PBDEs in the order: BDE 47 > BDE 100 > BDE 99 and BDE 49, which are the primary components of the Penta-BDE formulation, similarly to other reports from aquatic environment⁶. Eels had a higher contribution of BDE 47 ($\pm 60\%$) and lower contribution of BDE 99 ($\pm 6\%$) than the Penta-BDE mixture. This can be explained by either a preferential debromination of BDE 99 with the formation of BDE 47 as reported by several other studies⁷⁻⁹ or by differences in biomagnification factors among the PBDE congeners¹⁰.

Temporal variation

Comparing the eel samples collected from 2006 with eel collected from the same locations⁴ in 2000, an overall descending trend in PBDE contamination can be observed. BDE 47 contributes in both studies most to the total sum of PBDEs (see above), but its concentration has been reduced by more than a factor 50 (28 700 vs. 500 ng/g lw). Based on these results we can conclude that PBDE contamination of the investigated aquatic system seems to be lower than 6 years ago. HBCD was also susceptible to a decrease in contamination, but to a lesser extent (33 000 vs. 10 100 ng/g lw).

Comparison with other studies

A study by Covaci et al.¹¹ investigated the levels and distribution of PBDEs in zebra mussels and several freshwater fish species (also including eel) from different sites in Flanders, Belgium. One location (near Ghent) seemed to be more contaminated with an average sum PBDEs of 14 ng/g wet weight (ww), while other locations seemed to be less contaminated, with the sum PBDEs ranging between 2.0 and 3.6 ng/g ww. Eel samples from our low contaminated areas (L1 and L2) contained sum PBDEs between 0.9 and 2.69 ng/g ww, respectively. Eel samples from L4 to L7 contain sum PBDEs between 77 and 176 ng/g ww, respectively.

A study by Bragigand et al.¹² monitored PBDE levels in aquatic food webs from French estuaries. Eel samples were collected in the Loire and the Seine and PBDE congeners 28, 47, 99, 100, 153 and 154 were measured. The average sum PBDE congeners in eel samples from these locations were 0.6 and 5.0 ng/g ww. The most contaminated river shows concentrations that correspond to our reference areas, whereas our highly contaminated locations seem to contain 30 times higher PBDE levels.

Human exposure through dietary intake of eel

Exposure through eel consumption originating from L1 (reference area) and L5 are compared. Assuming that a normal weight adult consumes an average of 2.87 g eel daily¹³, an adult would be exposed to 3 ng PBDE/day if eel originates from L1, whereas he would be exposed to 327 ng PBDE/day if eel originates from L5 (factor 100 difference). The mean and median calculated dietary intake of PBDEs of the average population from different food groups based on PBDE concentrations measured in food and food frequencies are presented in Table 1. The contribution from eel caught in the contaminated area exceeds the other food groups by more than 20 orders of magnitude.

	Sum PBDEs (ng/day)	Reference
Fish and seafood	14	14
Meat products	15	14
Cheese	6.5	14
Eggs	5.1	14
Butter	4.1	14
Fast food	2.4	14
Eel location 1	3	This study
Eel location 5	327	This study

Table 1. Estimated dietary intake from different food groups (ng/day) in Belgium.

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