Occurrence of HBCDs, TBBPA, brominated phenols and their derivative in foodstuffs in Belgium

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Introduction

Brominated flame retardants (BFRs) are anthropogenic chemicals that are added to a wide variety of consumer products to improve their fire resistance. Hexabromocyclododecanes (HBCDs), 3,3',5,5'-tetrabromobisphenol A (TBBPA), and brominated phenols (BPs) and their derivatives constitute an important and widely used group of BFRs. Most of BRFs are not bound to the polymer by chemical binding, and may therefore leach from the products into the environment (Lyche et al., 2015). Due to their persistence and potential to biomagnification in living organisms and bioaccumulation in the food chain, BFRs may cause adverse effects in humans and animals. Food has been identified as the major source of exposure to BFRs for humans (Lyche et al., 2015). HBCDs, TBBPA, BPs and their derivatives are not regulated so far under specific EU regulations for food.
There is a lack of information on the occurrence data of the different BFRs in food which has hampered completion of intake assessment by the European Food Safety Authority (EFSA). This study was undertaken to respond to the Commission Recommendation 2014/118/EU on the monitoring of BFRs in food in Europe (Commission Recommendation, 2014). Food products commonly consumed in Belgium were analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) to investigate the occurrence of the following BFRs: α-1,2,5,6,9,10-hexabromocyclododecane (a-HBCD), β-1,2,5,6,9,10-hexabromocyclododecane (b-HBCD), γ-1,2,5,6,9,10-hexabromocyclododecane (g-HBCD), TBBPA, tetrabromobisphenol S (TBBPS), 4-bromophenol (4-BP), 2,4-dibromophenol (24 DBP), 2,6-dibromophenol (26-DBP) and 2,4,6-tribromophenol (246-TBP).

Materials and methods

Individual food samples were collected in Belgian supermarkets and local stores over a 2-year period (2015-2016). In total, 1289 individual food samples were combined to 183 composite samples, and these included fish and seafood, meat, dairy, egg and grain products, fats and oils, vegetables and food for infant and small children. The samples were ground and lyophilized (except for fats and oils).
For analysis of all target BFRs, except for TBBPS, 2.5 g lyophilized sample was weighed. Fifteen mL of hexane:DCM (1:1, *v/v*) was added, and the sample was vortexed, shaken for 20 min and centrifuged for 10 min at 4500 g. The supernatant was collected and evaporated till approx. 2 mL and cleaned-up using acidified silica (AS) (44%). Elution was done with 25 mL DCM. The sample was evaporated till near dryness, and ACN was added until a total volume of 100 µL.

For analysis of TBBPS, 2.5 g lyophilized sample was weighed. Fifteen mL of ACN:HCOOH (9:1, *v/v*) was added, and the sample was vortexed, shaken for 10 min and centrifuged for 10 min at 4500 g. EMR-Lipid kit (Agilent Technologies) was used for the clean-up. The supernatant was evaporated till dryness and reconstituted in 120 µL ACN.
The BFRs were measured on an ACQUITY UPLC system coupled to a Xevo-TQ-S mass spectrometer (Waters) operated in ESI(-) mode. Chromatographic separation was achieved on an ACQUITY UPLC BEH C18 column (1.7 µm, 100 x 2.1 mm) with an ACQUITY UPLC BEH C18 VanGuard pre-column (1.7 µm, 5 x 2.1 mm) (Waters). A gradient elution mode with mobile phase consisting of H_2O and ACN, both containing 0.1 % CH_3COOH, was used.

Results and discussion

The LC-MS/MS analysis revealed that 33% of food composites were contaminated with the target BFRs to some extent. The BFR content in all foodstuffs ranged from '<LOQ' to 16 ng/g ww (4-BP in canned king crabs) with an average content of 65 pg/g ww and the median of '<LOQ'. The highest number of detects (72%) was observed in the group 'Fish and fish products', while the groups 'Grains and grain products', 'Potatoes and derived products' and 'Animal and vegetable fat' were free from the BFRs. Distribution of the BFR concentrations in the Belgian foodstuffs is presented in Fig. 1.

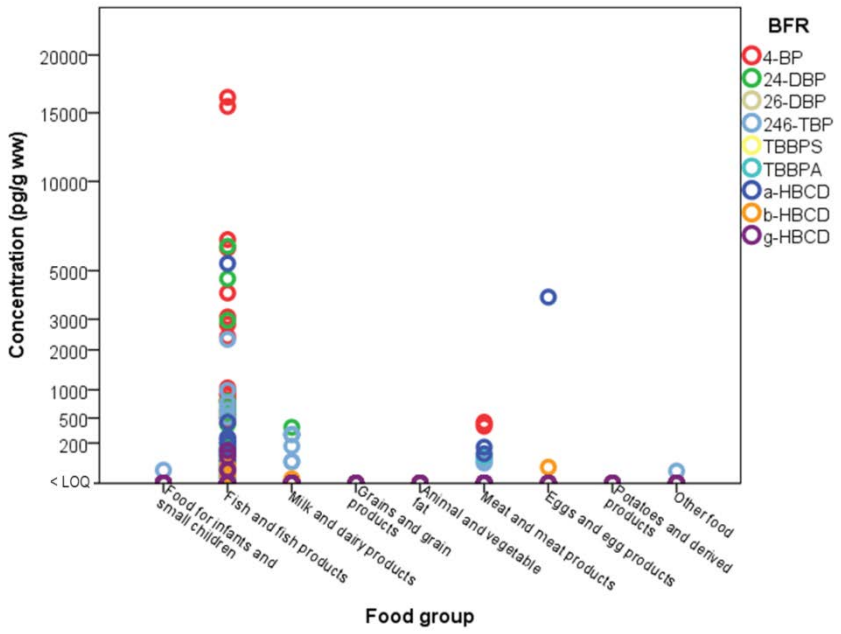

Fig. 1. Distribution of the BFR concentrations in the Belgian foodstuffs.

In all foodstuffs, the most frequently occurring BFR was 246-TBP followed by 4-BP and 24-DBP. 26-DBP and TBBPS were not detected in any of the food categories under study.
Of the HBCDs, a-HBCD was the most frequently detected and was most predominant in 'Fish and fish products' with the highest level of 5.3 ng/g ww in eel. Interestingly, a relatively high level of a-HBCD (3.8 ng/g ww) was measured in organic eggs, while the remaining egg samples (non-organic chicken and quail eggs) were negative. Regarding the group 'Food for infants and small children', only one sample out of 18 (6%) was contaminated and contained 246-TBP at low level. A number of BFRs were quantifiable in some samples from the groups 'Milk and dairy products' and 'Meat and meat products' being

mostly detected in cheese and desserts, and in some processed meat products and liver, respectively.

Acknowledgements

Financial support from the Belgian Federal Public Service (FPS) Health, Food Chain Safety and Environment (project RT 14/12 FLAREFOOD) is acknowledged.

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