Occurrence of halogenated flame retardants in Belgian foodstuffs

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Introduction

Halogenated flame retardants (HFRs) are man-made chemicals that are added to a wide range of consumer products to reduce their flammability. Because most HFRs are not chemically bonded to the products which they are added to, they can easily leach into the environment, ending up in air, sediments, biota, and food products for human consumption (de Jourdan et al. 2014; Bakker et al. 2008; Voorspoels et al. 2007).

Dietary intake is known to be one of the main routes of human exposure to HFRs, together with ingestion of indoor dust and inhalation of indoor air (Domingo 2012). Yet, the data scarcity regarding the presence of brominated FRs (BFRs) in food can lead to an incorrect estimation of the health risks and consequently of the exposure to HFRs *via* diet (as recently indicated by the European Food Safety Authority, EFSA 2011). For this reason, the EU adopted a Recommendation on the monitoring of BFRs in foodstuffs (Commission Recommendation 2014/118).

The main aim of this study was to follow-up on this Recommendation, providing data on HFR occurrence and levels in the main food categories consumed in Belgium. The presence of polybrominated diphenyl ethers (PBDEs), novel BFRs (hexabromobenzene (HBB), bis(tribromophenoxy)ethane (BTBPE), tetrabromobenzoate (TBB), tetrabromophthalate (TBPH)), tribromoanisole (TBA), and dechlorane plus (syn-DP and anti-DP) was assessed in about 200 composite food samples.

Materials and methods

To obtain a realistic profile of the Belgian dietary pattern, several food categories (including fish and seafood, meat, dairy products, eggs, grains, animal and vegetable fats, vegetables, and food for infants) were sampled over a two-year period (2015-2016) from Belgian supermarkets and local stores. The analytical method for the quantification of PBDEs and other HFRs in the considered food categories was previously optimized and validated (Poma et al. 2016). Briefly, for the quantification of HFRs in the food items, a variable amount of food sample (from 0.2 to 2 g dry weight, depending on the lipid content) was extracted through solid-liquid extraction using acetonitrile:toluene (9:1, *v/v*) solvent mixture. As lipids and pigments were co-extracted, a two-step clean-up (including Florisil and acid silica 5% *w/w*) was performed to efficiently remove these interferences prior to GC-MS analysis in electron capture negative ionization mode (GC-ECNI/MS)

The mass spectrometer was operated in selected ion monitoring (SIM) for the quantification of all the analytes of interest (BDE-28, -47, -49, -99, -100, -138, -153, -154, -183, -209, TBPH, TBB, BTBPE, HBB, TBA, syn-DP, and anti-DP). BDE-103 and BDE-128 were used as IS for the quantification of PBDE congeners (except BDE-209), TBA, HBB, and BTBPE. ^{13}C-BDE-209 was used as IS for BDE-209, while ^{13}C-TBB, ^{13}C-TBPH, ^{13}C-syn-DP, and ^{13}C-anti-DP, were used as IS for TBB, TBPH, syn-DP, and anti-DP, respectively.

Results and discussion

Among the considered HFRs, PBDEs were the most frequently detected compounds in all composite food samples, and were predominant in fish/seafood samples, with values up to 5,727 pg/g ww (fresh eel). BDE-47 was the most present congener in the fish category, followed by BDE-28, BDE-100, and BDE-154. Regarding the other food categories, BDE-47 and BDE-209 were the only congeners

detected in cheese and other dairy products, food for infants, eggs, grains, and potatoes, up to 81 pg/g ww and 16,839 pg/g ww, respectively. Apart from the fish/seafood category, only the meat composite samples showed detectable levels of BDE-28, measured up to 265 pg/g ww in veal tongue.

Regarding the other HFRs, only TBA was frequently detected in the food/seafood composite samples (median concentration of 508 pg/g ww), likely because it is naturally produced by algae, bacteria, fungi and sponges in the marine environment (Moore et al. 2002). Lower, but quantifiable, levels of TBA were also measured in meat, meat stocks, cereals, eggs, and cheese (up to 252 pg/g ww). However, because TBA was also present in non-negligible amounts in the procedural blanks, it is likely that these latter values resulted from activities related to the laboratory analysis (sample handling, presence in the lab environment), rather than from a real contamination of the samples. TBPH was only measured in vegetable oils (maximum level of 350 pg/g ww) and foie gras duck (202 pg/g ww). The other targeted HFRs were either not detected or below the LOQ in the analyzed food items.

Liquid milk, crustacean and vegetable samples showed levels of HFRs (including PBDEs) <LOQ.

Acknowledgments

The financial support was provided from Federal Public Service (FPS) Health, Food Chain Safety and Environment, project RT 14/12 FLAREFOOD, and from the University of Antwerp.

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