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Dietary intake of hexabromocyclododecane diastereoisomers (α-, β-, and γ-HBCD) in the Belgian adult population

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ABSTRACT

A study was performed to assess exposure of the Belgian population to HBCD diastereoisomers. Measurements of HBCD were performed by UPLC-MS/MS, on 45 composite samples from 5 major food groups: dairy (products), meat (products), eggs, fish (products) and a group of "other" products. The medium bound estimated average daily intake (EDI) of ΣHBCD in the Belgian population was 0.99 ng kg^{-1} bw d^{-1}. The diastereoisomer contribution to the mean EDI showed a predominance of γ-HBCD at 67%, followed by α-HBCD at 25% and 8% for β-HBCD. These results are consistent with the pattern found in the two food groups contributing the most to the EDI: meat (products) and the group of "other" products. Anyway, it has to be noted that diastereomeric distribution of HBCD can change due to bioisomerisation in biological material. Levels of HBCD diastereoisomers found in Belgian food samples of animal origin were low in comparison with those found in other EU countries and the resulting EDI was substantially below the proposed thresholds.

1. Introduction

HBCD is a highly lipophilic and additive brominated flame retardant (BFR), which is used in a variety of materials including synthetic polymers, electronic equipment, plastics, textiles and building materials, to prevent them from caching fire. Commercial HBCD is a mixture of 1, 2, 5, 6, 9, 10 hexabromocyclododecane isomers and consists mainly of γ-HBCD (70%) and two other diastereoisomers in lower amounts: β- and α- at 16% and 13% respectively (de Wit, 2002; UNEP, 2009). The restriction on the production and use of penta- and octa-bromodiphenyl ethers in Europe appears to be compensated by an increased use of the commercial HBCD (EFSA, 2006). This is reflected by an ongoing increase of the HBCD levels in the environment as reported by Law et al. (2006a). In addition, various monitoring studies have indicated its presence in wildlife and in humans making it a ubiquitous contaminant (Covaci et al., 2006).

From a toxicological point of view, HBCD has the potential to adversely affect the environment and human health.

For humans, extrapolation of test results done on mammals indicate several effects on three different locations in the body: thyroid (Hamers et al., 2006), liver (Kling and Förlin, 2009), and nervous system (Eriksson et al., 2006). The preponderance of evidence from available studies indicates that HBCDs lack significant genotoxic potential *in vitro* as well as *in vivo* (ECB, 2008).

The presence of HBCD (all isomers) in a wide range of matrices, its suspected toxic effects and continuous massive use may indicate a public health concern. One of the many sources of human exposure to HBCD is exposure through the diet. Surprisingly, little information is available regarding HBCD levels in foods and therefore, not many dietary intake assessments were published previously. To our knowledge, there were no studies done yet on dietary exposure to these compounds in Belgium. The aim of this study was to assess the dietary intake of HBCD in the Belgian adult population and to get insight into the diastereoisomer pattern of that exposure.

2. Materials and methods

2.1. Food consumption data

Consumption data from the Belgian national food consumption survey of 2004 were used to perform the exposure assessment. Aims, design and methods of this survey are described elsewhere (De Vriese et al., 2005; Vandevijvere et al., 2009). The target population comprised all Belgian inhabitants of 15 years or older. The final sample included 3245 participants randomly selected from the National Register using a multi-stage stratified procedure. Information on dietary intake was collected by two non-consecutive

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24 h recalls in combination with a food frequency questionnaire. During the 24-h recall interviews, the respondents reported the quantity of all foods and beverages consumed during the preceding day.

The 24 h recalls were performed using EPIC-SOFT, a validated software package (Slimani and Valsta, 2002). This program, allows one to obtain very detailed information about the foods consumed and the recipes used in a standardized way.

2.2. Food sampling

Food samples were purchased during autumn 2008 from the five most frequented supermarkets and at some fish and butcher's shops in Brussels. Since Belgium is a small country, no distinction was made between the different regions.

Only food products containing fat of animal origin were taken into account (meat and meat products, fish and fish products, eggs, dairy products and some other products such as cakes and cookies). A total of 549 food items were purchased, based on their frequency and amount of consumption as reported in the food consumption survey of 2004. One composite sample of vegetable oil and one composite sample of choco spread, containing high quantities of vegetable oils/fats, were also analyzed to evaluate if the processing and/or transportation add any HBCDs to these foods.

The samples were homogenized and mixed in order to prepare 42 composite samples as presented in Table 1. Except for milk and eggs which were stored at 4 °C, the other samples were kept at −20 °C.

As much as possible, the percentage of each food item within the composite sample reflected the proportions of intake as described in the Belgian food consumption survey. Four food groups of animal-origin were subjected to HBCD analysis as is shown in Table 1: (1) dairy products including milk, organic milk, 4 country cheeses (Belgian, Dutch, French, Italian), goat cheese and butter; (2) meat and meat products, including pork, sheep, beef, duck, rabbit, turkey, horse, chicken, organic chicken, free range chicken, game, liver products and meat preparations (without liver); (3) eggs, including battery eggs, eggs from free range hens and organic eggs; (4) fish and fishery products, including salmon, tuna, cod, herring, sardine, mackerel, other fishes (trout, eel, sardine, lute, perch, sole), molluscs including mussels, oysters and scallop shell and crustaceans including crab and shrimp, (5) and other products including animal deep frying fat, croissants, cakes, pies, pastries, cookies, pizzas, vegetable oils and chocolate spreads.

2.3. Reagents and chemicals

Solvents used were HPLC-grade and purchased from Biosolve. Sulfuric acid (analytical reagent grade) and sodium sulfate anhydrous were purchased from J.T. Baker (B) and Silica gel 60 (mesh 70–230) from Fluka (B). Analytical standard stock solutions were obtained from Wellington Laboratories (UK) at individual concentration of 50 μg mL^{-1} in toluene with purity >98%: native (α-, β-,

Table 1
Composition of the composite samples.

Dairy and dairy products	Meat and meat products	Eggs	Fish and fish products	"Other" products
Milk (19)	Beef (10)	Battery (10)	Salmon (14)	Animal deep frying fat (4)
Organic milk (8)	Veal (10)	Free range hens (10)	Tuna (10)	Croissant (20)
Belgian cheese (23)	Pork (10)	Organic (10)	Cod (10)	Cake, pies, pastry (30), Cake (25%), tart (75%)
Dutch cheese (10)	Sheep (10)		Herring (8)	Biscuit (30)
French cheese (23)	Turkey (10)		Sardine (7)	Pizza (10)
Italian cheese (17)	Horse (10)		Mackerel (8)	Vegetable oil (25) *Olive oil (43%), arachide oil (6%), sunflower oil (4%), salad oil (1%), corn oil (3%), margarine (43%)*
Goat cheese (10)	Chicken (10)		Other fishes (16) *Trout (56%), halibut (15%), sole (11%) monkfish (10%), saithe (6%), hake (3%)*	Chocó spread (9)
Butter (12)	Duck (10)		Crustaceans (12) *Scampi (35%), crab (18%), crayfish (9%), shrimp (30%), prawn (8%)*	
	Rabbit (10)		Molluscs (10) *Mussels (83%), oyster (10%), scallop shell (7%)*	
	Game (18) *Hind (19%), pheasant (20%), guinea hen (21%), wild boar (11%), quail (12%), pigeon (17%)*		Fishery product salads (9) *Tuna salad (33%), crab salad (22%), fish salad (22%), surimi salad (22%)*	
	Mixed meat preparations & products (23) *Sausages (41%), salami (21%), pie (14%), meatloaf (17%), pudding (1%), horse filet (5%)*		Other fishery products (14) *Fish stick (33%), surimi (66%)*	
	Liver and liver products (10) *Liver of veal (34%), pork (18%), rabbit (23%), foie gras (25%)*			
	Organic and free range chicken (10) *Organic chicken (50%), free range chicken (50%)*			

() Number of samples per composite sample is given in brackets.