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Food risk assessment for perfluoroalkyl acids and brominated flame retardants in the French population: Results from the second French total diet study

G. Rivière [a,*], V. Sirot [a], A. Tard [a,1], J. Jean [a], P. Marchand [b], B. Veyrand [b], B. Le Bizec [b], J.C. Leblanc [a]

[a] French Agency for Food, Environmental and Occupational Health & Safety, 27-31 Avenue du général Leclerc, F-94701 Maisons-Alfort Cedex, France
[b] LUNAM Université, Oniris, LABERCA, Nantes F-44307, France

HIGHLIGHTS

- Contaminations of PFAAs and BFRs in foods representing French population habits.
- Exposures to PFAAs and BFRs lower than those reported elsewhere in Europe.
- Dietary exposures to PFAAs and BFRs revealed no risk for these compounds.

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ABSTRACT

To determine the exposure of the French population to toxic compounds contaminating the food chain, a total diet study was performed in France between 2007 and 2009. This study was designed to reflect the consumption habits of the French population and covered the most important foods in terms of consumption, selected nutrients and contribution to contamination. Based on French consumption data, the present study reports the dietary exposure to perfluoroalkyl acids (16 congeners) and brominated flame retardants (polybrominated diphenyl ethers, hexabromocyclododecane and polybrominated biphenyls). Comparison of the calculated dietary exposures with the generally accepted health-based guidance values revealed that most compounds do not pose any risk. There are however knowledge gaps for some congeners in these large chemical classes.

1. Introduction

Perfluoroalkyl acids (PFAAs) are a large class of chemical contaminants of anthropogenic origin that includes perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These substances are highly stable (having high thermal, chemical and biological resistance) owing to their strong carbon–fluoride bonds. They are amphiphilic, and therefore have surfactant properties. They are used in numerous industrial applications and common consumer products: stain- and water-resistant treatments (clothes, rugs, carpets and furniture), non-stick coatings (kitchen utensils, paper including food packaging) and certain specialised applications (cosmetics, fire-fighting foam, plant protection products).

However, contrary to many persistent halogenated compounds (e.g. polychlorinated biphenyls (PCBs)), they do not accumulate in adipose tissues. Some PFAAs such as PFOS and PFOA persist in the environment and can accumulate in animals and humans. High concentrations are generally observed in the liver, blood and kidneys. Toxicity studies on PFAAs generally only investigate PFOS and PFOA (Olsen et al., 2007). Their apparent elimination half-lives in humans are approximately 4 to 5 years (Olsen et al., 2007). The main toxic effects reported in animals have been observed in the liver (Seacat et al., 2003; Thomford, 2002 in EFSA, 2008), on reproductive and developmental functions and immune and hormonal systems (Seacat et al., 2002) as well as on lipid metabolism (EFSA, 2008). PFOS and PFOA have neoplastic effects but have not shown to be genotoxic (Thomford, 2002 in EFSA, 2008). The tolerable daily intake (TDI) level generally accepted for PFOS is 150 ng/kg body weight (bw)/day based on the effects on lipid and thyroid hormone levels observed in a 6 month toxicology study in monkeys (EFSA, 2008). For PFOA, the accepted TDI is 1.5 μg/kg bw/day based on a two-generation toxicology study showing some maternal hepatotoxicity (EFSA, 2008). In a prospective study of a birth cohort from the National Hospital in the Faroe Islands, PFAAs were associated

* Corresponding author at: ANSES, 27-31 Avenue du général Leclerc, F-94701 Maisons-Alfort Cedex, France.
E-mail address: gilles.riviere@anses.fr (G. Rivière).
[1] Present address: Food Additives and Nutrient Sources (ANS) Unit, European Food Safety Authority, Largo N. Palli 5/a, I-43121 Parma, Italy.

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with a reduced humoral immune response to routine childhood immunisations in children (Grandjean et al., 2012).

PFAAs contaminate several compartments of the environment (water, soil, air) and accumulate in the food chain (Kowalczyk et al., 2012). Food, particularly seafood products, is a significant source of exposure to PFAAs in humans (Cornelis et al., 2012; EFSA, 2008; Trudel et al., 2008).

Brominated flame retardants (BFRs) are chemical substances incorporated in the plastic parts of electronic devices and electronic circuits to give them fire-retardant properties. They are also present in foams and padding materials (domestic and industrial), car and aircraft interiors and some textiles. This class encompasses numerous structurally different compounds, including hexabromocyclododecane (HBCD), polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs) (209 congeners, chemically related to PCBs).

Due to their wide use, BFRs have become widespread environmental pollutants. Consequently, the general population is exposed to these compounds by numerous routes (food, dust and through inhalation, etc.); however, food appears to be the main route of exposure for some BFRs such as PBDEs (Domingo, 2012; Frederiksen et al., 2009).

In laboratory animals, BFRs have been shown to have toxic effects particularly on hepatic, hormonal, reproductive, nervous and immunological functions. Some of these compounds accumulate in the body. Although carcinogenicity data are still limited, PBDEs, PBBs and HBCDs have not shown to be genotoxic.

The characterisation of chronic human toxicity of BFRs is difficult since they are often experimentally studied as mixtures. In its opinion on PBBs, the European Food Safety Authority (EFSA) could not define a health-based guidance value, but suggested comparing data on exposure to PBBs with a no observed adverse effect level (NOAEL) of 0.15 mg/kg bw/day observed in rats (induction of hepatic carcinomas) (EFSA, 2010). However, EFSA indicates that this NOAEL corresponds to a worst-case situation because it is based on a study using a technical PBB mixture, the congener composition of which was not a representative of the congener profiles present in food.

Regarding PBDEs, seven to eight congeners are generally chosen for experimental studies. In 2006, the French Food Safety Agency (AFSSA) concluded that it was not possible to define a health-based guidance value (AFSSA, 2006) while the Joint FAO/WHO Expert Committee on Food Additives (JECFA) considered that no harmful effects can occur in rodents after oral exposure to PBDE-47 and PBDE-99 (known to be the most toxic) at levels lower than 100 μg/kg bw/day (JECFA, 2006). Given that the chemical structure of PBDEs is similar to that of non-dioxin-like polychlorinated biphenyls (NDL-PCBs), their modes of action should be similar (Kodavanti et al., 2005). Due to their common mechanism of action (Miller et al., 2012; Pellacani et al., 2012) and pending the definition of a health-based guidance value for PBDEs, the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) Expert Committee on food contaminants compared exposure to the eight PBDEs with the threshold of 10 ng/kg bw/day defined by AFSSA in 2007 for the six NDL-PCBs that are the most frequently found in food (AFSSA, 2007). Recently, EFSA set up benchmark dose lower confidence limits (BMDLs) for a benchmark response of 10% ($BMDL_{10}$) for the four most "of concern" BFR compounds based on their neurodevelopmental effects: 309 μg/kg for BDE-47, 12 μg/kg bw for BDE-99, 83 μg/kg bw for BDE-153 and 1700 μg/kg bw for BDE-209 (EFSA, 2011a). Elimination kinetics differ considerably between experimental animals and humans for most PBDE congeners. Consequently, EFSA recommends converting $BMDL_{10}$ values into estimated human intakes associated with the body burden at the $BMDL_{10}$ (resulting figures are 172 ng/kg bw for BDE-47, 4.2 ng/kg bw for BDE-99, 9.6 ng/kg bw for BDE-153 and 1.7 mg/kg bw for BDE-209). Ratios between exposure and these values were recommended by EFSA as the basis for further risk assessment.

Regarding HBCDs, EFSA identified neurodevelopmental effects on behaviour as the critical endpoint, and derived a $BMDL_{10}$ of 0.79 mg/kg bw. Due to the limitations and uncertainties in current knowledge, EFSA concluded that it was inappropriate to use this BMDL to establish a health-based guidance value, and instead recommended using the margin of exposure (MOE) approach for the risk characterisation of HBCDs by comparing dietary intake for HBCDs with the estimated human intake associated with the body burden at the $BMDL_{10}$, which has been calculated using a one-compartment pharmacokinetic model at steady-state and set at 0.003 ng/kg bw/day.

The objectives of the present study were to assess the risk to the French population related to the presence of PFAA and BFR compounds in food. Exposures were calculated using concentrations of 16 PFAAs, 8 PBDEs, 3 PBBs and 3 HBCDs measured in food samples collected for the second total diet study (TDS) performed in France (Sirot et al., 2009).

2. Materials and methods

2.1. Food sampling

Selected core foods were the representative of the French population diet. The selection was based on the results of the second individual and national study on food consumption survey, INCA 2 (Dubuisson et al., 2010; Lioret et al., 2010).

The foods consumed most by adults and/or children were selected (consumer rate of at least 5%). In addition, the main known or assumed food contributors of the substances included in this study were also selected (if not already selected by the first criterion). The core foods ($n = 212$) covered about 90% of the whole diet of adults and children, and were divided into 41 food groups.

Sampling was performed between June 2007 and January 2009 in eight large regions in mainland France (33 cities), and each food collected in a region was sampled during two different seasons, when possible.

To be as representative as possible of the French food consumption habits, each food sample was composed of up to 15 subsamples of equal weight of the same food, considering market share, origin, species, processing and packaging, flavouring, etc. Altogether, around 20,000 products or subsamples were purchased, then prepared "as consumed" according to French cooking practices, e.g. vegetables and fruits were mainly washed and peeled, meat and seafood were cooked (braised, pan-fried, grilled, baked, deep-fried, etc.). For each food, the 15 subsamples were frozen, pooled and cryomilled, and 1319 composite samples were ultimately analysed. More details about the methodology can be found in Sirot et al. (2009).

2.2. Sample analysis

2.2.1. Perfluoroalkyl acids

The analytical method was used to determine the concentration of 5 perfluoroalkyl sulfonates: PFOS, perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS) and perfluoro-1-decanesulfonate (PFDS), and 11 perfluorocarboxylic acids: PFOA, perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA) perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA) (Kadar et al., 2011). Solid food samples were freeze-dried and extracted with methanol. After evaporation, food extracts were purified onto two consecutive solid-phase extraction (SPE) columns (copolymeric reversed phase and charcoal). Final purified extracts were analysed by liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS); electrospray ionisation in the negative ion mode was preferred and at least two