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Occurrence of perfluorinated alkylated substances in cereals, salt, sweets and fruit items collected in four European countries

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HIGHLIGHTS

- 12 Perfluoroalkyl acids were determined in fruits, cereals, sweets and salt.
- Food items were collected in four European countries.
- PFOA was the most abundant compound.
- The calculated dietary intake remain far below the tolerable levels.

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ABSTRACT

In the context of a European project, 12 perfluoroalkyl acids (PFAAs) were determined in 14 food items collected in four European countries representing northern, southern, eastern and western Europe. This study presents the results of PFAAs measured in fruit, cereals, sweets and salt. Out of the 12 PFAAs, 10 PFAAs were detected in 67% of the samples. Overall, PFOA was the most abundant compound and the highest concentrations were found for PFOS but all were less than 1 ng g^{-1}. When comparing the four countries, highest levels and detection frequencies were observed in Belgium (Western Europe), followed by the Czech Republic (Eastern Europe), Italy (Southern Europe) and finally Norway (Northern Europe). Comparison of profiles and levels is difficult due to variations in constitution of the food categories in the investigated countries and countries of origin of the food items. Dietary intake assessments for PFOS and PFOA show that the daily intake of PFAAs is far below the existing tolerable levels. However, they contribute to the total dietary intake and should therefore be included in future dietary exposure assessments.

1. Introduction

Perfluoroalkyl acids (PFAAs) are persistent organic pollutants with unique physico-chemical properties. Due to the strong C–F bond and both hydrophobic and lipophilic properties, PFAAs have been used in broad range of industrial applications and consumer products such as surfactants for lowering surface tensions, fire-fighting foams, floor polish, water- and oil repellents for textiles and additives for food contact paper (Kissa, 2001; Buck et al., 2011). As a consequence of their widespread use, persistence and potential to bioaccumulate in the environment, PFAAs are globally detected in wildlife and humans. The presence of PFAAs in serum or blood from non-occupationally exposed humans is well documented (reviewed by Fromme et al., 2009). The ingestion of dust, dermal adsorption, inhalation via air and dietary intake have been described as possible exposure routes for the general population (D'Hollander et al., 2010; Cornelis et al., 2012; Klenow et al., 2013). The intake through the diet and water has been reported by several papers as one of the most important intake routes (e.g. Fromme et al., 2009; Vestergren and Cousins, 2009). In recent years the literature on PFAAs in food and/or dietary intake has increased rapidly but data necessary to estimate the intake via food remain scarce (Ericson et al., 2008; Ericson-Jogsten et al., 2009;

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Noorlander et al., 2011; Cornelis et al., 2012; Vestergren et al., 2012b; Klenow et al., 2013). However, PFAAs in food items in which high levels are expected such as fish, seafood, organs (liver) and meat products are described in the literature (D'Hollander et al., 2010; EFSA, 2012). Likewise, data in water and/or drinking water are relatively abundant (D'Hollander et al., 2010; Eschauzier et al., 2011). On the other hand, sufficient data on other food items such as cereals, fruits, vegetables, fats, sugar-rich products and processed food are occasionally described even though they are consumed in high amounts (Ericson et al., 2008; Noorlander et al., 2011; Vestergren et al., 2012b). This could be explained by the lack of reliable sensitive analytical methods which are required to detect PFAAs at the pg g^{-1} levels. Furthermore, the complexity of the food matrices plays a major role in the extraction and analysis of PFAAs (van Leeuwen et al., 2009). Recently, suitable sensitive methods to achieve these goals have been published (Ballesteros-Gómez et al., 2010; Ullah et al., 2012; Vestergren et al., 2012a). Dietary intake assessments have been published earlier but the uncertainties of most of these studies are rather high due to the high limits of quantification (LOQs) and/or to the limited amount of analysed food items.

The calculation of the dietary intake of PFAAs is not straightforward and apart from the direct intake of PFAAs, involves the intake of precursor compounds that potentially can degrade to PFAAs contributing to the total dietary intake (Vestergren et al., 2008; Ullah et al., 2014). In this study, the additional intake of precursor compounds is not taken into account.

The contamination of fruit, cereals, sweets and salt can occur via atmospheric deposition, uptake from crops via soil or water but also via processing, packaging or food preparation (Domingo, 2012; Gebbink et al., 2013; Xu et al., 2013). The current literature on dietary exposure is difficult to interpret and hard to compare as the studies differ in sampling design (food basket, duplicate diet, 24 h recall) and in analytical performance. If the analytical methods applied are not sensitive enough, most of the PFAAs analysed are reported as below LOQ which results in great variety between upper and lower bound (UB and LB, respectively) approaches for the exposure estimation.

In order to enable a direct comparison between European data on perfluorinated alkylated substances the European Union project PERFluorinated Organics in Our Diet (PERFOOD, FP7-KBBE, Grant agreement No. 227525, www.perfood.eu) adopted a harmonised integrated approach in designing the sampling plan and applied high analytical quality and low method detection limits. Within the PERFOOD project the present study focused on four out of fourteen collected categories, i.e. cereals, sweets (sugar and honey), salt and fruits. The PFAA concentrations and the dietary intake estimation for such food items are presented in this work. Studies by Herzke et al. (2013) and Hlouskova et al. (2013) report the results for vegetables and food items of animal origin, respectively, and, together with a detailed exposure estimation study by Klenow et al. (2013) describe the overall aims, sampling procedures and handlings within the PERFOOD project.

2. Materials and methods

2.1. Sampling

The sampling plan for the PERFOOD project was based on the different food consumption data from European countries whereby the regional differences in dietary items are taken into account in order to estimate the exposure of the European population to PFAAs. Therefore four countries were selected for collecting the food items i.e. Norway, the Czech Republic, Italy and Belgium representing northern, eastern, southern and western Europe according to the Country Assignments to GEMS/Food program (WHO, 2003). Sampling took place between spring and summer 2010.

The selection of food items was based on several equally important criteria described by Herzke et al. (2013): (1) relevance of the intakes for the selected European area, (2) lack of data on PFAA concentrations in food, and (3) practicability of the sampling strategy according to human, instrumental and budgetary resources available within the PERFOOD project. For the PERFOOD project, food items representing 14 categories suggested by EFSA (EFSA, 2011a) were sampled. The current paper focuses on four categories i.e. cereals, sweets (sugar and honey), salt and fruits. An overview of the sampled items in each region is given in Table 1. Items were collected and registered according to the guidance document provided by EFSA (EFSA, 2010). The individual items were randomly selected in three national retail stores covering different brands or countries of origin per item. Of each item, three to ten single lots were sampled for the preparation of the pool, depending on the availability present in the stores. If 1–3, 4–10 or more than 10 lots or brands are present in the stores, the number of lots to compose a pool should be 3, 5, 10 or >15 respectively. For the cereals and sweets at least 200 g of each selected brand was sampled. For fruits 2–4 individual items of each lot were sampled to represent one lot. For grapes and strawberries respectively, 200 and 250 g were taken. To simplify a harmonised sampling and sampling handling in all four regions, a detailed sampling manual was applied by the four partners involved in the sampling (NILU, Tromsø, Norway; Institute of Chemical Technology, Prague, Czech Republic; Istituto Superiore di Sanità, Rome, Italy; University of Antwerp, Belgium). This sampling manual was based on the Annex I to Commission Regulation (EC) No 1883/2006 of 19 December 2006 laying down

Table 1
Overview of the number of individual items collected to compose a pooled sample in the Czech Republic, Belgium, Norway and Italy for cereals, sweets and fruit and the number of pooled samples (n) that were analyzed for the representative items.

Representative part Sampling country	East EU Czech Republic	West EU Belgium	North EU Norway	South EU Italy	n
Cereals					
Rice	–	10	–	4	2
Wheat (white)	3	5	13	5	4
Oats	–	3	–	9	2
Rye	9	–	–	–	1
Sweets					
Sugar (beet)	3	5	–	3	3
Sugar (cane)	–	–	5	–	1
Honey	15	10	17	3	4
Fruits					
Berries					
Strawberries	3	3	2	–	3
Citrus fruit					
Oranges	3	10	5	–	3
Tangerines	3	–	–	–	1
Lemons	–	3	6	–	2
Grapefruits	–	–	–	2	1
Pipe and stone fruit					
Apples	15	5	10	6	4
Pears	3	3	2	4	4
Peaches	3	–	–	9	2
Plumes	–	5	–	9	2
Others and exotic fruit					
Melons	3	–	9	–	2
Grape	–	5	–	5	2
Bananas	–	–	–	6	1
Miscellaneous					
"Rock" salt	9	–	13	–	2
"Marine" salt	–	–	–	4	1

–; Not sampled