Environmental Research 134 (2014) 345–352

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Determination of contamination pathways of phthalates in food products sold on the Belgian market

Mirja Van Holderbeke [a], Lieve Geerts [a], Guido Vanermen [a], Kelly Servaes [a], Isabelle Sioen [b,c], Stefaan De Henauw [b,d], Tine Fierens [a,b,*]

[a] Flemish Institute for Technological Research (VITO), Boeretang 200, B-2400 Mol, Belgium
[b] Ghent University, Department of Public Health, Faculty of Medicine and Health Sciences, De Pintelaan 185, B-9000 Ghent, Belgium
[c] Research Foundation Flanders (FWO), Egmontstraat 5, B-1000 Brussels, Belgium
[d] University College Ghent, Department of Nutrition and Dietetics, Faculty of Health Care "Vesalius", Keramiekstraat 80, B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form
13 August 2014
Accepted 14 August 2014

Keywords:
Phthalates
Belgium
Food
Contamination pathways
Bread
Concentration profiles

ABSTRACT

As numerous studies have indicated that food ingestion is the most important exposure pathway to several phthalates, this study aimed to determine possible contamination pathways of phthalates in food products sold on the Belgian market. To do this, concentrations of eight phthalates (dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), benzylbutyl phthalate (BBP), dicyclohexyl phthalate (DCHP), di(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP)) were determined in 591 foods and 30 packaging materials. In general, the four most prominent phthalates in Belgian food products were DEHP, DiBP, DnBP and BBP. Special attention was given to the origin of these phthalates in bread, since high phthalate concentrations (especially DEHP) were determined in this frequently consumed food product. Phthalates seemed to occur in Belgian bread samples due to the use of contaminated ingredients (i.e. use of contaminated flour) as well as due to migration from phthalate containing contact materials used during production (e.g. coated baking trays). Also the results of the conducted concentration profiles of apple, bread, salami and two cheese types revealed the important role of processing – and not packaging – on phthalate contents in foods.

1. Introduction

Phthalates (diesters of *ortho*-phthalic acid) are a group of organic lipophilic chemicals with a wide range of user applications. They are primarily used as plasticisers to increase the flexibility of polymer products and can be present in printing inks, lacquers, building materials, pharmaceutical products (e.g. enteric-coated tablets) and medical devices (e.g. blood bags and tubings). Due to their widespread use, phthalates are omnipresent in the environment (Cao, 2010; Fromme et al., 2007a; Wittassek et al., 2011; Wormuth et al., 2006).

Over the last decades, phthalates have attracted public attention due to their possible harmful effects to human health (Hauser and Calafat, 2005; Meeker et al., 2009; Shea, 2003). For example, some phthalates and their metabolites have been reported to adversely affect the male reproductive system (Meeker et al., 2009) and to have the potential to alter androgen-responsive brain development in humans (Swan et al., 2010). Of all exposure pathways, food intake is the most important one for phthalates, followed by dust ingestion and indoor air inhalation (Clark et al., 2011; Fromme et al., 2007b; Rudel and Perovich, 2009; Wormuth et al., 2006).

Between 2009 and 2011, a Belgian research project (acronym: PHTAL) was conducted by order of the Belgian Federal Public Service of Health, Food Chain Safety and Environment with the following main objectives:

- To obtain accurate and sensitive data of phthalates in all kinds of food products and packaging materials sold on the Belgian market;
- To gain a clear understanding of possible contamination pathways of phthalates in the Belgian food market;
- To estimate dietary exposure to phthalates in the Belgian population.

In this PHTAL project, eight frequently used phthalate compounds were considered: dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), benzylbutyl

* Corresponding author at: Flemish Institute for Technological Research (VITO), Boeretang 200, B-2400 Mol, Belgium.
E-mail address: tine.fierens@vito.be (T. Fierens).

http://dx.doi.org/10.1016/j.envres.2014.08.012
0013-9351/

phthalate (BBP), dicyclohexyl phthalate (DCHP), di(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP).

The first and third objectives of the PHTAL project have been published recently by Fierens et al. (2012) and Sioen et al. (2012), respectively. To investigate the occurrence of phthalates in food products and packaging materials on the Belgian market (i.e. the first objective), an analytical procedure was developed and validated for the determination of eight phthalate compounds of interest in various types of foods and packaging materials. Subsequently, a first screening measurement campaign (MC1) was conducted between 2009 and 2010, in which the phthalate compounds were analysed in 388 food products and 12 packaging materials. Sample selection for MC1 was based on consumption data from the most recent Belgian national food consumption survey (De Vriese et al., 2005) and the likelihood that foodstuffs contain phthalates. During MC1, DEHP was observed to be the most abundant phthalate compound, followed by DiBP, DnBP and BBP. In food products, concentrations of DEHP were generally also the highest of all considered phthalate compounds. DEHP levels above 1000 μg/kg fresh weight were among other things determined in bread, vegetable oil, (goat's) cheese and fish products. In packaging materials on the other hand, DiBP concentrations were the highest, especially in cardboard (Fierens et al., 2012).

To have an idea of the dietary phthalate exposure in the Belgian population (i.e. the third objective), the analysed phthalate concentrations in foods were linked to data from two Belgian food consumption surveys: one for preschool children (Huybrechts et al., 2008) and one for adults (De Vriese et al., 2005). For both preschool children and adults, dietary intake of DEHP was the highest, followed by DiBP. The estimated intake values of DEP, DnBP and BBP were far below the tolerable daily intake (TDI) values (EFSA, 2005a; 2005c; WHO, 2003). However, for DEHP, the 99th percentile of the intake distribution of preschoolers in the worst case scenario was equal to 80% of the TDI (EFSA, 2005b). Bread was observed to be the most important contributor to dietary DEHP exposure in the Belgian population (Sioen et al., 2012).

This paper describes the results of the second research objective of the PHTAL project, namely the determination of contamination pathways of phthalates in food products sold on the Belgian market. Thereto, a second, more oriented measurement campaign (MC2) was conducted, in which 203 extra food products and 18 extra packaging materials were analysed. The sample selection of MC2 was mainly based on the measurement results of MC1: food products, in which high phthalate contents were determined (e.g. bread) and were investigated in more detail. Food products not considered in MC1, but necessary to assess dietary intake (e.g. eggs, coffee and vegetarian food) were analysed in MC2 as well.

2. Material and methods

2.1. Sample collection

MC2 of the PHTAL project was carried out between 2010 and 2011. During this campaign, 203 additional food products and 18 additional packaging materials were purchased from various Belgian shops. Samples were collected in order to (1) gain more insight into possible contamination pathways of phthalates in the Belgian food chain, especially of the food items that contained high phthalate concentrations in MC1 of the project (e.g. bread) (Fierens et al., 2012) and (2) to complete the concentration database to correctly assess the dietary intake of phthalates in the Belgian population (Sioen et al., 2012). Information regarding brand name, packaging material and properties, fat content, shelf life, time and place of purchase, picture and – if relevant – product specific properties (e.g. pH and preserving agents) of food were stored in a database. An overview of the sample selection of MC2 is given in Table 1. For comparison, the numbers of samples collected during MC1 of the PHTAL project (Fierens et al., 2012) are also mentioned.

Besides giving an overview of the general analytical results of the food groups additionally considered in MC2 (i.e. wine, coffee and tea, vegetarian food (i.e. meat substitutes), eggs and boiling water), two topics were investigated in this study in more detail for the four most detected phthalate compounds, namely (1) concentrations in bread: different types of bread, different providers, different packaging materials, concentrations in bread ingredients versus bread, and so on, and (2) concentration profiles in different food items (e.g. salami, goat's cheese and apple).

2.1.1. Bread

In MC1, it was demonstrated that bread samples had a relatively high DEHP content, i.e. DEHP levels up to 1073 μg/kg were noticed (Fierens et al., 2012). Because of large share of bread in the food consumption pattern of children and adults (Devriese et al., 2006; Vanhauwaert, 2012), additional bread products were bought in MC2 of the PHTAL project in order to investigate possible contamination sources. Of all bread products analysed in both MC1 and MC2 ($n=62$), 43 bread samples were investigated in more detail. These bread samples were purchased from different locations spread over Belgium and were originating from supermarket chains as well as from fresh bakeries. Parameters that were explored in these 43 bread samples were: flour type (white ($n=21$) versus brown/wholemeal ($n=22$)), packaging type (paper ($n=32$) versus paper with plastic window ($n=5$) versus plastic ($n=6$)), location (nine fresh bakery locations ($n=20$) versus 12 supermarket locations ($n=23$)), form (long ($n=31$) versus round ($n=12$)) and contact time with bread bag (long/prepacked ($n=7$) versus short/packed at purchase ($n=36$)).

By comparing absolute phthalate contents of a bread bag with absolute phthalate contents of the bread samples that were packed in this bread bag, the role of the packaging material on phthalate contamination in bread could be investigated. For this purpose, phthalate concentrations were determined in two supermarket bread samples with high DEHP contents (i.e. 1002 and 1073 μg/kg fresh weight) as well as in the paper bag of these two bread samples. Subsequently, absolute phthalate contents in the bread bag and in two bread samples were calculated by multiplying the analysed concentrations by an assumed contact surface of 1200 cm² and a bread weight of 0.8 and 0.6 kg fresh weight, respectively.

To investigate whether phthalates may transfer from contact materials to bread during baking and/or whether phthalate contamination may arise from the ingredients used, three homemade bread samples were analysed as well as the flour mixes used to bake these breads. The first brown bread was baked in a bread machine with a coated metal baking tray using 500 g of an all-in bread mix (i.e. a mix of flour, flour treatment agent, ascorbic acid and enzymes) and tap water. The second wholemeal bread was baked in a blue-steel baking tray in a conventional hot-air oven after mixing 500 g of a wholemeal flour mix (flour, flour treatment agent, ascorbic acid), 30 g of margarine, dried yeast, salt and tap water. Mixing of these ingredients took place in a metal pot with a metal kneader. The third bread was baked in a metal baking tray coated with polytetrafluoroethylene in a conventional hot-air oven. This dark bread was composed of 500 g of a Black Forest flour mix (mixture of three kinds of flour), 30 g of margarine, yeast, salt and tap water. All three breads were unsliced prior to analysis. Just like in the previous mentioned investigation, absolute phthalate contents were calculated in order to compare phthalate contents in the bread and corresponding flour mix samples. To do this, the phthalate concentrations in the bread samples were multiplied by a weight of 0.8 kg and the phthalate levels in the flour mix samples were multiplied by a weight of 0.5 kg.

2.1.2. Concentration profiles

'Concentration profiles' of five different food products (apple, bread, soft goat's cheese, salami and semi-soft cheese) were made in order to investigate the origin of the phthalates detected (i.e. migration from contact materials, environmental transfer and/or the production process). Thereto, samples were taken from the surface and the core of apple and bread. Regarding soft goat's cheese, salami and semi-soft cheese, samples were taken from different places in the product as shown in Fig. 1. All samples were collected using a kitchen knife that was rinsed with dichloromethane (Merck, Overijse, Belgium) prior to sampling. Regarding the packaging materials of the investigated foods, apple was not packed and bread and salami were packed at purchase in a paper bag and in paper with a polyethylene lining, respectively. Soft goat's cheese was packed in a plastic printed tub with on the inside of the bottom, an extra metallic layer and the investigated semi-soft cheese was wrapped in wax with on the outside, an additional printed plastic layer.

2.2. Analytical procedure

The concentrations of DMP, DEP, DnBP, DiBP, BBP, DEHP, DCHP and DnOP in all food products and packaging materials of MC2 were analysed in the same way as samples analysed in MC1 of this project (Fierens et al., 2012). In brief, for the sample preparation, a distinction was made between high-fat foods (fat content of more than one per cent on a fresh weight basis), low-fat foods (fat content of less than one per cent), aqueous-based beverages and packaging materials. Of every high-fat food sample, 5–20 g was extracted with acetone/*n*-hexane (1:1; Merck, Overijse, Belgium) to obtain at least 0.5 g fat; for the extraction of low-fat foods, 10 g was used. For aqueous-based beverages, a liquid–liquid extraction with dichloromethane was applied using 500 ml of each sample. Packaging materials