Chemosphere 168 (2017) 692–698

Contents lists available at ScienceDirect

Chemosphere

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

Method development for assessing the human exposure to organophosphate flame retardants in hair and nails

Andreia Alves [a, b, *], Adrian Covaci [b], Stefan Voorspoels [a]

[a] Flemish Institute for Technological Research (VITO NV), Boeretang 200, 2400 Mol, Belgium
[b] Toxicological Centre, Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium

HIGHLIGHTS

- The exposure to four PFRs was assessed through hair, finger and toe nails analyses.
- Extraction performance of SPE Oasis Wax *versus* STRATA X-AW was tested.
- DBP reduction in the blanks was successfully achieved by a new wash step in SPE.
- DPhP was the major metabolite measured in finger and toe nails.
- Over 2 months, the female showed constant exposure to the parent PFR in finger nails.

ARTICLE INFO

Article history:
Received 6 May 2016
Received in revised form
17 October 2016
Accepted 2 November 2016
Available online 9 November 2016

Handling Editor: Andreas Sjodin

Keywords:
Organophosphate flame retardants
Diesters
Hair
Finger nails
Toe nails
Human exposure

ABSTRACT

In the present study, a new extraction method based on acid digestion and SPE clean-up (Oasis Wax) was developed for measuring four PFR metabolites (i.e. dibutyl phosphate (DBP), diphenyl phosphate (DPhP), bis(1,3-dichloro-2-propyl)phosphate (BDCPP) and bis(2-butoxy ethyl) phosphate (BBEP)) in hair and nails. The method optimization was done according to a combinatorial design (Taguchi) where several parameters were efficiently optimized. Precision was lower for hair than for nails (RSD % 18 and 28%). Recoveries were >74%. High DBP levels in procedural blanks were traced back to the use of SPE cartridges. Therefore a new SPE pre-treatment was tested, reducing significantly DBP levels (<1 ng).

Levels of the PFR metabolites were measured in scalp hair, finger, and toe nails collected over two months in two volunteers (female and male). DPhP levels were extremely high (in μg/g range) in both finger and toe nails in the female. BDCPP and BBEP were the minor metabolites detected in nails (average levels of 28–64 ng/g and <2.2–4.1 ng/g, respectively). DPhP was the only metabolite detected in hair (0.23–0.25 ng/g). Results showed that there is a possible contribution from both an external (via deposition) and an internal exposure, however it was not possible to fully understand their extent. Since there were no records of lifestyle and due to the small sample size, the major exposure source could not be addressed here. Nevertheless, there is evidence that hair and nails (finger and toe) might be good indicators of human exposure to PFRs, especially to TPhP.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Since the ban on the use of polybrominated diphenyl ethers (PBDEs) as flame retardants (FRs) in 2009 (Stockholm Convention on Persistent Organic Pollutants, 2009), an increasing use of alternative substances, such as the organophosphate triesters (OPEs or more commonly designated as phosphorous flame retardants (PFRs)) has been observed. In 2006, PFRs were already responsible for 20% of the FR consumption in Europe, against 10% of the total consumption by brominated flame retardants (BFRs) (Van der Veen and De Boer, 2012). In fact, PFRs have become suitable alternatives nowadays, especially after the restriction of BFRs in 2011 in Europe and the U.S. (Andrae, 2007; Bromine Science and Environmental Forum (BSEF),).

PFRs can be categorized in halogenated and non-halogenated where the halogenated and non-halogenated aryl PFRs are incorporated in many products as FRs (e.g. electronics, furniture,

* Corresponding author. Flemish Institute for Technological Research (VITO NV), Boeretang 200, 2400 Mol, Belgium.
E-mail address: andreia.alves@vito.be (A. Alves).

http://dx.doi.org/10.1016/j.chemosphere.2016.11.006
0045-6535/© 2016 Elsevier Ltd. All rights reserved.

textiles), while non-halogenated alkyl PFRs are mostly used as plasticizers and antifoaming agents (e.g. polymers, paints, varnishes, lacquers and hydraulic fluids) (Van der Veen and De Boer, 2012; Andresen et al., 2004). Many PFRs are additives, therefore they are not chemically bound to the products, which may facilitate their release to the environment. Due to their widespread use, PFRs can now be detected in air (Hartmann et al., 2004), dust (Van den Eede et al., 2011; Abdallah and Covaci, 2014), sediment (García-López et al., 2009), water (Andresen et al., 2004), animals and in humans (Van der Veen and De Boer, 2012).

After human uptake, they are quickly metabolized to form dialkyl or diaryl diester phosphates, which can be detected in urine (Van den Eede et al., 2013a; Cequier et al., 2014; Möller et al., 2004; Cooper et al., 2011; Hoffman et al., 2014; Reemtsma et al., 2011; Van den Eede et al., 2015; Dodson et al., 2014; Petropoulou et al., 2016) or in human milk (Sundkvist et al., 2010). Recent studies, conducted by Kucharska et al. (2014, 2015a, 2015b). and Liu et al. (2015) have suggested the use of other non-invasive matrices in exploring human exposure to PBDEs and PFRs via hair and/or nails, although there is still no information about the suitability of these matrices to reflect internal exposure.

To our knowledge, there is no literature that elucidates the human exposure to PFRs or their metabolites using nails. In addition, this is not yet totally explored for hair, where the assessment has been done so far only for the parent PFRs (Kucharska et al., 2014, 2015a,b). In hair, usually an acid digestion (e.g. HNO_3, H_2SO_4, HCl) or combination with hydrogen peroxide (H_2O_2) precedes the SPE clean-up (Kucharska et al., 2014, 2015a,b; Liu et al., 2015), assumed enabling the release the PFRs from the matrix.

Previous studies indicated that SPE based on anion exchange interactions, such as Oasis Wax (Van den Eede et al., 2013a) or Strata X-AW (Cooper et al., 2011; Hoffman et al., 2014; Van den Eede et al., 2015; Petropoulou et al., 2016) are suitable to extract PFR metabolites from biological matrices. After activation with an acidified solvent, these sorbents contain positively charged groups that can interact with the analytes. Afterwards, a base (e.g. NH_4OH) is used to elute the target compounds. In addition, some authors reported on direct analysis of urine samples by LC-MS without using any extraction or clean-up procedure (Cequier et al., 2014; Reemtsma et al., 2011). For obvious reasons this approach cannot be used for hair and nails as extraction is necessary.

To understand whether it is possible to evaluate the internal exposure to PFRs via hair and nails, this study was focused on PFR metabolites. A set of synthetized standards (native and labelled internal standards) enabled quantitative determination. A new extraction method was optimized using a combinatorial design (Taguchi). Relevant parameters of the developed solid phase extraction (SPE)-based method, such as column conditioning, pH and removal of background contamination were optimized. The method was validated and applied on scalp hair (one sample), and finger and toe nails (multiple samples) collected from two individuals (female and male) over a two months.

2. Materials and methods

2.1. Chemicals and standards

Dialkyl and diaryl phosphate standards including bis(1,3-dichloro-2-propyl)phosphate (BDCPP), bis(2-butoxy ethyl) phosphate (BBEP) and the deuterated internal standard (IS) solutions (BBEP-d_4 and BDCPP-d_{10}) were custom synthesized by Dr. Vladimir Belov (Max Planck Institute, Göttingen, Germany). Purity of the standards was higher than 98% as confirmed by MS and NMR techniques (data not shown). Dibutyl phosphate (DBP), diphenyl phosphate (DPhP) and the IS DPhP-d_{10} were supplied by Sigma-Aldrich (Bornem, Belgium). Since there is no DBP labelled standard available, IS DPhP-d_{10} was used as DBP IS. The stock and the spiking solutions were prepared in methanol. The stock calibration standard solutions were prepared in water. The working calibration standards were prepared by diluting an appropriate volume of each individual stock solution (metabolites and IS) in methanol.

Oasis Wax cartridges (60 mg, 30 μm, 3 mL) and Strata X-AW (60 μm, 3 mL) were purchased from Waters (Millford, MA, USA) and Phenomenex Inc (Torrance, CA, USA), respectively. Ammonium hydroxide solution (NH_4OH, > 25%) and ammonium acetate (NH_4Ac, 99%) were obtained from Sigma Aldrich (Diegem, Belgium). Formic acid (HCOOH, 99%), nitric acid (HNO_3, 65%) and sodium hydroxide pellets (NaOH) were supplied by Merck (Darmstadt, Germany). The ultra-pure water was obtained from a Milli-Q ultrapure water system (Advantage A10 system, Overijse, Belgium). Methanol (MeOH) was of analytical grade (Fisher Scientific, Loughborough, UK).

2.2. Hair and nails sampling

Hair and nail samples were collected from two adult volunteers (male and female) that gave their consent to participate in the study (Ethical approval register N.° B300201316329). The sampling took place over approximately two months, where the volunteers collected both finger (n = 9) and toe (n = 6) nails. The total weight of finger and toe nails collected from the female participant were 0.24 and 0.22 g, respectively. The male participant collected 0.22 and 0.12 g, respectively. At the end of the sampling period, one hair sample (from each volunteer) was collected near the root and only the scalp segment was analyzed (<5 cm) (Papadopoulou et al., 2016). Hair and nails were stored at room temperature until analysis.

For the method development, pooled nail samples (whole or grinded) were prepared from different individuals recruited within our institute, while for hair a large portion was collected in distinct periods from one individual with short hair (length < 5 cm), and therefore used as pool sample. Prior to extraction, the nail samples were rinsed with acetone to remove residues of nails polish. Hair samples were not washed or decontaminated, once according to Kucharska et al. (2015a) there is no suitable washing medium able to entirely and exclusively remove external contamination from hair surface.

2.3. Method development

2.3.1. Optimization of SPE clean-up

One hundred mg of hair and thirty mg of nails (powder and whole) were spiked with PFR metabolites (15–20 ng) and IS (15 ng). Firstly, an acid digestion was promoted by the nitric acid (2 mL, 10% (m/v)) in ultrasound (30 °C, 30 min), in order to release the compounds from the matrices. Afterwards, two SPE extraction procedures (Oasis Wax or Strata X-AW) were tested. Before the SPE, the pH of the hair/nail's extracts was adjusted to pH 6-8 adding NaOH (6 N). Prior loading the analytes on the Oasis Wax and Strata X-AW and in order to activate the sorbents, the cartridges were conditioned with MeOH (2 mL) and acidified water (2 mL of 1% HCOOH in water (*v/v*)). Then, the samples were loaded onto the SPE and the interferences were washed out using 2 mL of acidified water and 2 mL MeOH (for Oasis Wax protocol) or using 2 mL NH_4Ac (25 mM) adjusted to pH 6.8 following by drying the cartridge (5–10 min) under vacuum (for Strata X-AW protocol) (Phenomenex,). The elution of the target analytes was achieved using 2 mL of NH_4OH solution prepared in MeOH (5%, *m/v*). The extracts were evaporated under a gentle N_2 flow (and below 50 °C). The residue was resuspended in 100 μL of H_2O:MeOH (65:35, *v/v*).

Download English Version:

https://daneshyari.com/en/article/5746611

Download Persian Version:

https://daneshyari.com/article/5746611

Daneshyari.com