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Bioaccessibility of PBDEs present in indoor dust: A novel dialysis membrane method with a Tenax TA® absorption sink

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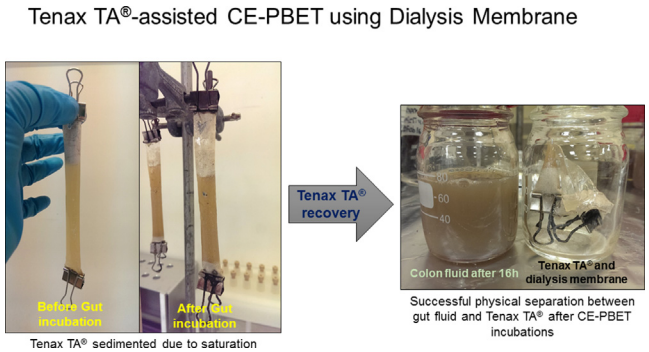
HIGHLIGHTS

- First method employing dialysis membrane for physical separation between Tenax TA® and dust
- Tenax TA® used as an absorption sink trapped in dialysis membrane mimics the situation *in vivo*
- CE-PBET performance was tested under different Tenax TA® loadings (0.25, 0.5 & 0.75 g)
- Two to three-fold bioaccessibility increase with Tenax TA® inclusion for all PBDEs
- Similar colon sorption to Tenax TA® in small intestine for BDE28, but higher than small intestine sorption for other PBDEs

GRAPHICAL ABSTRACT



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ABSTRACT

Human uptake of flame retardants (FRs) such as polybrominated diphenyl ethers (PBDEs) *via* indoor dust ingestion is commonly considered as 100% bioaccessible, leading to potential risk overestimation. Here, we present a novel *in vitro* colon-extended physiologically-based extraction test (CE-PBET) with Tenax TA® as an absorptive "sink" capable to enhance PBDE gut bioaccessibility. A cellulose-based dialysis membrane (MW cut-off 3.5 kDa) with high pH and temperature tolerance was used to encapsulate Tenax TA®, facilitating efficient physical separation between the absorbent and the dust, while minimizing re-absorption of the ingested PBDEs to the dust particles. As a proof of concept, PBDE-spiked indoor dust samples ($n = 3$) were tested under four different conditions; without any Tenax TA® addition (control) and with three different Tenax TA® loadings (*i.e.* 0.25, 0.5 or 0.75 g). Our results show that in order to maintain a constant sorptive gradient for the low MW PBDEs, 0.5 g of Tenax TA® are required in CE-PBET. Tenax TA® inclusion (0.5 g) resulted in 40% gut bioaccessibility for BDE153 and BDE183, whereas greater bioaccessibility values were seen for less hydrophobic PBDEs such as BDE28 and BDE47 (~60%). When tested using SRM 2585 ($n = 3$), our new Tenax TA® method did not present any statistically significant effect ($p > 0.05$) between non-spiked and PBDE-spiked SRM 2585 treatments. Our study describes an efficient method where due to the sophisticated design, Tenax TA® recovery and subsequent bioaccessibility determination can be simply and reliably achieved.

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1. Introduction

Despite the strict legislative measures on the use of Penta-BDE and Octa-BDE formulations in both the EU and USA in consumer products (*e.g.* carpets, electronic appliances and furniture polyurethane foam) (Dodson et al., 2012; European Commission, 2003) and their listing as persistent organic pollutants (POPs) under the Stockholm Convention (Stockholm Convention, 2009a, 2009b), polybrominated diphenyl ethers (PBDEs) are legacy flame retardants (FRs) being detected in considerable levels in indoor dust from China (Cao et al., 2014; Sun et al., 2016), France (Raffy et al., 2017), the UK (Kademoglou et al., 2017; Tao et al., 2016), the Czech Republic, USA and Canada (Venier et al., 2016). Under this regime, human health concerns remain a critical issue, given the well-known PBDE potential to induce endocrine and thyroid disruption (Legler, 2008) and neurodevelopmental disorders in children (Bellinger, 2013; Costa and Giordano, 2007).

Total pollutant concentration of a contaminated solid matrix is perceived as the bioavailable fraction after ingestion and it is frequently used in human risk and exposure assessment (Semple et al., 2004). However, the assumption that 100% of the ingested toxicant within a matrix being available is unrealistic (Collins et al., 2015). Animal bioavailability studies (*e.g.* rodents or swine) are representative of the *in vivo* situation, but are often hindered due to financial and ethical restrictions (Oomen et al., 2003; Ruby et al., 2002). To avoid risk overestimation, bioaccessibility, *i.e.* the maximal fraction of an organic pollutant released from an ingested matrix (*e.g.* dust) into the gastro-intestinal tract (GIT) fluids of the organism has been proposed as a more realistic but conservative approach in human exposure assessment of persistent organic pollutants (POPs), serving as a surrogate to bioavailability (Brandon et al., 2006; Dean and Ma, 2007; Oomen et al., 2000). Several physiologically-based extraction tests (PBET) have been proposed to assess organic pollutant release and uptake from an ingested matrix *via* the GIT fluids *in vitro* (Brandon et al., 2006; Cave et al., 2010; Gouliarmou and Mayer, 2012; Tilston et al., 2011; Van de Wiele et al., 2004), as a substitute to *in vivo* studies (James et al., 2011) or for high-throughput estimates of bioaccessibility when animal studies are not feasible (Rodríguez-Navas et al., 2017; Ruby et al., 1996). Due to the non-polar and hydrophobic nature of hydrophobic organic compounds (HOCs) such as PBDEs, sorption to indoor dust is likely to occur *via* volatilisation, abrasion or fragmentation (Cao et al., 2014; García-Alcega et al., 2016) marking dust ingestion as a potential major route of exposure to FRs for humans (Alves et al., 2014; Jones-Otazo et al., 2005). Hence, *in vitro* bioaccessibility studies have been deployed, assessing human exposure to contaminated indoor dust on a wide spectrum of HOCs including brominated flame retardants (BFRs) (Abdallah et al., 2012), organophosphate FR (OPFRs) (He et al., 2016; Quintana et al., 2017), pesticides and polychlorinated biphenyls (PCBs) (Ertl and Butte, 2012) and polybrominated diphenyl ethers (PBDEs) (Yu et al., 2012). However, the lack of an adsorption sink in the various test formats may lead to risk underestimation due to the absence of constant concentration gradient (Collins et al., 2015). Sink conditions better mimic the sorption/desorption processes in the human GIT *in vivo* and, coupled with the lipid-rich environment of the GI lumen and a long matrix:fluid contact time, may improve the bioaccessibility estimates of HOCs, such as PBDEs (Collins et al., 2015; Zhang et al., 2015, 2016).

A colon-extended PBET system (CE-PBET) with a carbohydrate-rich colon compartment as a "sink", favouring polycyclic aromatic hydrocarbons (PAHs) desorption from soil has been described (Tilston et al., 2011). Strong adsorbents such as silicone-activated contaminant traps, cyclodextrins and silicone rods have also been proposed as "absorption sink" materials in PBET systems, to improve bioaccessibility estimates for PAH-contaminated soil and biochar (Gouliarmou et al., 2013; Mayer et al., 2016; Zhang et al., 2015). As part of the International Organization for Standardization (ISO) guideline on bioavailability, an extended (20 h) Tenax-based extraction method achieved increased mobilisation (*i.e.* bioaccessibility) of HOCs from soils and sediments onto this infinite sink and has been proposed for standarisation (ISO, 2015; Ortega-Calvo et al., 2015). Tenax TA® is a versatile absorption sink with large surface area and high sorption capacity for HOCs and was thus used as an "infinite" sink in PBET systems, studying the uptake of FRs and PAHs *via* indoor dust (Fang and Stapleton, 2014) and soil (Li et al., 2015), respectively. Cornelissen et al. (1997) employed Tenax TA® studying sorption/desorption kinetics of PAHs, alkylbenzenes and PCBs from dredged sediments; the sink captured the organic pollutants from the solid matrix but the Tenax TA® beads adhered to the glassware with consequent problems for physical separation and recovery of Tenax TA® from the matrix (Cornelissen et al., 1997). The variability in Tenax TA® mass recovery, its separation from the matrix and the design of an appropriate vessel for Tenax TA® inclusion (*e.g.* stainless steel net) during PBET incubation has discouraged further applications of Tenax TA® in environmental exposure studies (Li et al., 2016; Mayer et al., 2016). In the work presented here, we describe a novel *in vitro* method capable to overcome the aforementioned challenges concerning physical separation and recovery of Tenax TA® from the matrix, while facilitating its successful inclusion and performance as an adsorption sink in a previously established bioaccessibility test, namely CE-PBET, for the assessment of oral bioaccessibility of PBDEs from indoor dust.

To separate aqueous and solid matrices, a regenerated cellulose (RC) dialysis tubing method was employed, studying the sorption and dissolution of perchloroethane and PAHs from clay-rich materials and sewage sludges, respectively (Allen-King et al., 1995; Woolgar and Jones, 1999). RC membranes present high pH and temperature tolerances, carry no fixed charge and are highly resistant to halogenated hydrocarbons, such as PBDEs (Pollard, 1987). Tubing characteristics including length, width, membrane sealing method and molecular weight cut off (MWCO) have been evaluated. For example, 2.5 g of contaminated sewage sludge were introduced into 10 cm of dialysis tubing with a 3.5 kDa MWCO (Woolgar and Jones, 1999). Alternatively, 20 cm of dialysis tubing (29 mm width; 12–14 kDa MWCO) was used to ensure that at least 30% of the analyte mass would remain in the solid phase after equilibration (Allen-King et al., 1995). The solid material in the tubing was then introduced inside glass bottles with synthetic groundwater spiked with the HOCs of interest. During equilibration, all non-settling particles were retained inside the dialysis membrane, while dissolved organic pollutants could permeate through the membrane and equilibrate across the dialysis tubing by passive diffusion (Allen-King et al., 1995).

Our study aims are to systematically (a) develop an efficient method to separate Tenax TA® and indoor dust as a matrix whilst enabling desorption of PBDEs to the Tenax TA® and (b) optimise Tenax TA® as an absorption sink for PBDEs in a colon-extended gastro-intestinal bioaccessibility *in vitro* system (CE-PBET).

2. Materials and methods

2.1. Target analytes and indoor dust

An indoor dust sample was collected in 2013 from a pre-existing vacuum cleaner bag in an office at Reading (UK) and was used during method development tests and the results are presented in Sections 3.1 and 3.2. The dust sample was sieved to <250 μm, a particle cut off likely to be ingested by humans (Yu et al., 2012), using a hexane-washed, metallic sieve and stored in hexane-washed, amber glass bottles at +4 °C. Concentrations of all target analytes in all dust samples were determined using methods described elsewhere (Kademoglou et al., 2017). Briefly, 30 mg of dust was extracted with 2.5 mL hexane:acetone (3:1) using ultra-sonication extraction for 10 min and vortexing for 1 min three times. The combined extract was concentrated to 1 mL and loaded on aminopropyl (NH_2) silica cartridges (500 mg, 3 mL, Agilent, USA) and further eluted with 10 mL hexane. The eluate