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## ORGANOPHOSPHORUS FLAME RETARDANTS IN SWEDISH HOUSE DUST

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### Introduction

The addition of flame retardants efficiently reduces the flammability of materials and products. Brominated organic flame retardants such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have been widely used for decades. However, due to their toxicity and persistence in the environment, their use is nowadays banned or restricted (Stockholm Convention on POPs). This has resulted in increased use of alternative flame retardants, such as organophosphorus flame retardants (OPFRs), which are also used as plasticizers and stabilizers and found in a various products such as building materials, electronics and furnishing materials (Wypych 2004).

Given that OPFRs are incorporated in such a variety of materials and products, sampling of dust provide a good matrix to assess the overall exposure of OPFRs in the indoor environment. Inhalation and dermal contact to dust has also been identified as an important exposure pathway for flame retardants to humans (Lorber et al. 2008) and small children in particular, given their frequent hand-to-mouth activity (Stapleton et al. 2008).

The aim of this study was to determine the concentration of OPFRs in house dust from Swedish homes within the framework of the MISSE project. MISSE is investigating the mixtures of several endocrine disrupting chemicals (EDCs) in the indoor environment, with special focus on thyroidogenic compounds. Several studies have found correlation between OPFR exposure and thyroidogenic effects (Meeker and Stapleton 2010, Kim et al. 2015). The indoor dust analyzed here are part of a larger set of target analysis reported elsewhere (Norrgran Engdahl et al. in preparation).

### Materials and methods

#### Samples

Indoor dust samples from Swedish homes were collected using a Dustream™ dust collector (Indoor Biotechnologies Ltd., Wiltshire, United Kingdom) containing a disposable filter (mesh size 40 µm) attached on a household vacuum cleaner tube. Fifteen individual dust samples collected from living rooms and three samples containing dust collected from living room and bedrooms, were analysed along with indoor house dust (SRM 2585) purchased as standard reference material from the US National Institute of Standards and Technology (NIST, Gaithersburg, USA).

#### Chemicals and standards

Tri(isobutyl) phosphate (TiBP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl)phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPP), 2-ethylhexyl diphenyl phosphate (DPEHP), tris(2-ethylhexyl) phosphate (TEHP) were purchased from Chiron AS (Trondheim, Norway), AccuStandard, Inc. (New Haven, USA) and Sigma-Aldrich (Steinheim, Germany) and used as authentic reference standards. Deuterium-labelled TCEP used as surrogate standard was purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA). Tri-n-pentyl phosphate (TPEP) was purchased from AccuStandard, Inc. (New Haven, USA) and used as volumetric standard.

#### Extraction and clean up

House dust (50 mg) was extracted and fractionated according to a slightly modified method by Van den Eede et al. (2012). Prior to extraction deuterium-labelled TCEP was added as surrogate standards to each sample. Shortly described; the extraction was performed using 2mL iso-hexane:acetone (3:1, v/v), vortexed (1 min) and ultrasonicated (10 min). After centrifugation (10 min, 3000 rpm), the liquid phase was transferred to a new test tube and the pellet re-extracted twice as described. The liquid phases from each extraction cycle were combined (6 mL) and evaporated to near dryness under a gentle stream of

nitrogen and reconstituted in 0.5 mL iso-hexane. Each sample was then fractionated on a Florisil SPE cartridge which had been pre-cleaned with 10 mL iso-hexane before applying the sample. A fraction (F1) containing PBDEs and PCBs was eluted with 10 mL iso-hexane and saved for future analysis. The OPFRs were then collected by elution with 10 mL ethyl acetate in a second fraction (F2). This fraction was gently evaporated to near dryness under a gentle stream of nitrogen and reconstituted in in toluene (0.5 mL). Prior to instrumental analysis, TPEP was added as volumetric standard. The samples were transferred to vials and the final sample volume adjusted to 100  $\mu$ L by evaporation.

#### Instrumental analysis

The samples were analysed using a gas chromatograph coupled to a nitrogen phosphorous detector (GC-NPD, Agilent 6890). The GC-NPD was equipped with a PTV injector and an auto sampler (Agilent 7693). The injector (held at 300°C) was operated in splitless mode and the analytes were separated on a DB5 capillary column (30 m x 0.32 mm i.d. x 0.25 $\mu$ m film thickness; J&W Scientific). The temperature program for the column oven was: 100°C for 1.5 min, 10°C/min to 270°C (2 min) and 20°C/min to 300°C (5min). Nitrogen gas was used as carrier gas at a constant flow of 1mL/min throughout the run. The NPD detector temperature was set at 350°C and nitrogen was used as makeup gas. Identification and quantification was performed using authentic reference standards.

#### QA/QC

A procedural solvent blank was extracted and cleaned up along with each batch of samples for quality control. None of the target compounds analysed were detected in the blank samples. The mean recovery of the surrogate standard was 109% (RSD 12%). The limit of detection (LOD) was set as the signal-to-noise ratio of 3. The limit of quantification was determined as the lowest calibration point which was reliably detected by the GC-NPD.

### Results and Discussion

Concentration of OPFRs present in dust from Swedish homes is presented in **Figure 1**. The total concentration of OPFRs ranged from 11 to 32  $\mu$ g/g dust. Interestingly, the composition of OPFRs differed greatly between samples and likely reflect different building materials, furniture and consumer products present in the represented homes. All target compounds except TiBP and TBP were present in all samples. TBOEP and TCIPP were found in highest concentrations (20 and 19  $\mu$ g/g dust, respectively). TBOEP is used in floor polishes and as a plasticizer in rubber and plastics (WHO 2000) whereas TCIPP is used in rigid and flexible polyurethane foams used for example in furniture upholstery (WHO 1998).

The applied analytical method for extraction and analysis of OPFRs in house dust was evaluated by use of standard reference material (SRM 2585). As no certified values exist for OPFRs, the measured concentrations were compared with two previous studies using the same reference material. The measured concentrations of OPFRs reported by Van den Eede et al. (2012) and Berg et al. (2010) using gas chromatography coupled to mass spectrometry (GC-MS) and the results obtained using GC-NPD in the present study are shown in **Figure 2**. The results were found to be overall in agreement except for one compound, TBOEP which was found at lower concentrations in the present study than previously reported. However, since the concentrations of TBOEP differ greatly in all three studies it is difficult to assess if the levels of TBOEP in this study are underestimated or not.

#### Conclusions and future perspectives

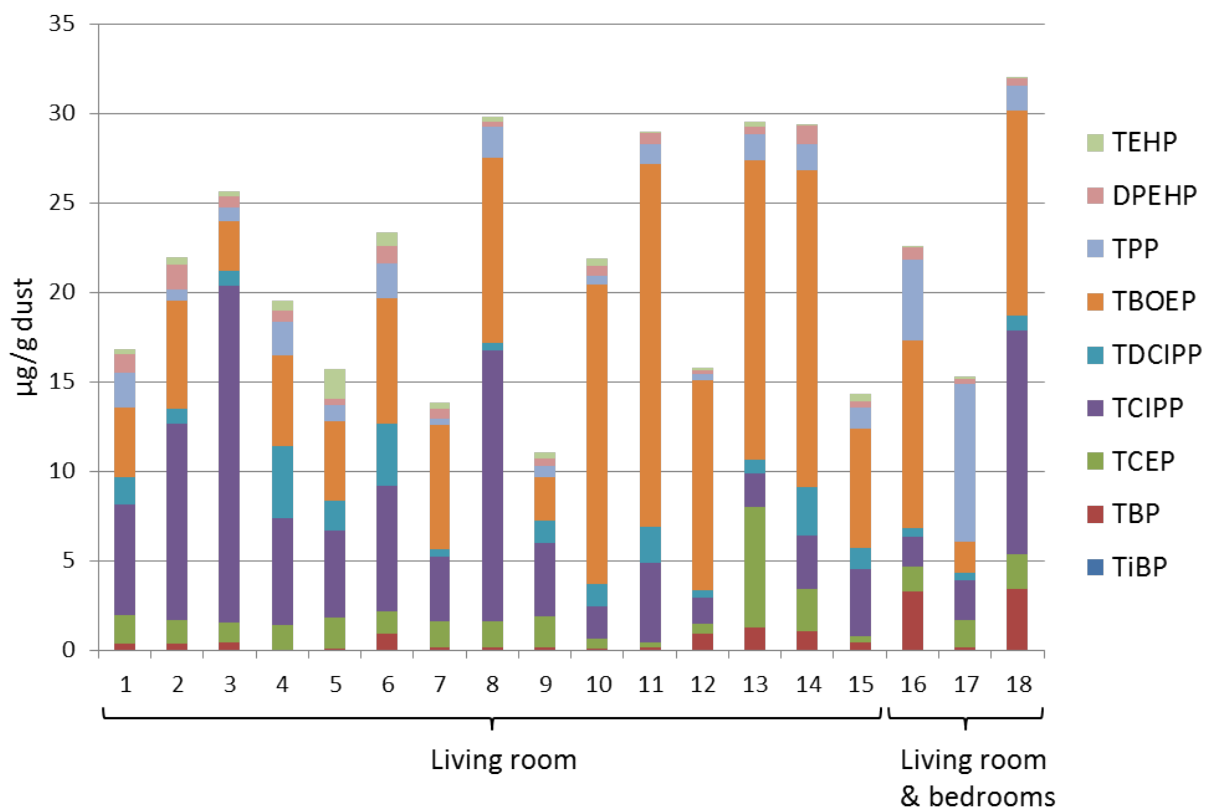
This study gave insight of concentrations and compound profile of OPFRs in house dust from Swedish homes. The samples were analyzed as part of the research project MISSE which aims to assess the exposure situation of anthropogenic thyroid hormone disrupting compounds in the indoor environment using cats as sentinels for human and child exposures to indoor related chemicals and to assess their thyroidogenic effects.

#### Acknowledgement

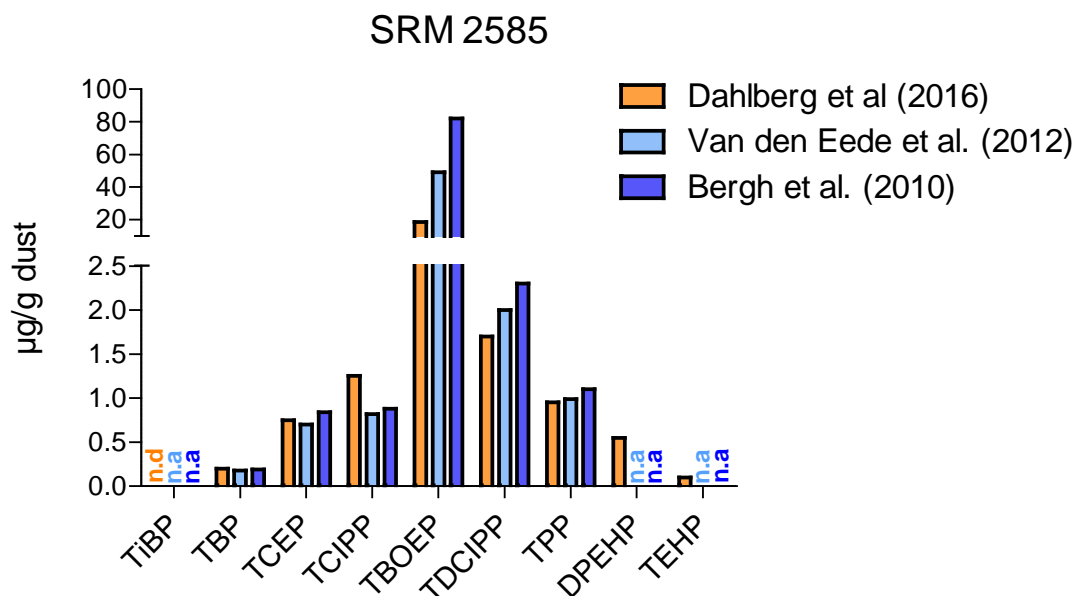
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**Figure 1.** Concentration of OPFRs (µg/g dust) in dust from Swedish homes.



**Figure 2.** Concentrations of OPFRs (µg/g dust) in standard reference material (SRM 2585) reported by three different studies.