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Occurrence of synthetic phenolic antioxidants and transformation products in urban and rural indoor dust☆

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ABSTRACT

In this study, seven synthetic phenolic antioxidant (SPA) analogues were positively found in urban and rural indoor dust samples collected from Shandong province in China, among which the novel 2,4,6-tri-*tert*-butylphenol (AO 246), 2,6-di-*tert*-butyl-4-sec-butylphenol (DTBSBP), 2,4-di-*tert*-butylphenol (DBP) and 4,4'-butylidenebis (2-(1,1-dimethylethyl)-5- methyl-phenol) (AO 44B25) analogues accounted for 29% of total SPA concentrations (∑SPAs). Urban dust showed significantly higher ∑SPA levels (range: 1.56e3 - 2.03e4 ng/g) compared with those in rural indoor dust (668–4.39e3 ng/g, $p < 0.05$). 2,6-Di-tert-butyl-4-methylphenol (BHT) was the dominate analogue in the urban indoor dust, which constituted of 74% in ΣSPAs. While, varied composition profiles of SPAs were noticed in rural indoor dust, for instance, AO 246 (46%) and BHT (43%) had similar contributions to ∑SPAs. Three BHT transformation products (TPs) were also detected in most of the urban and rural dust samples (>97%), with individual residue level in the same order: 2,6-di-*tert*-butyl-1,4-benzoquinone (BHT-Q) > 2,6-di-tert-butyl-4-hydroxy- 4-methyl-2,5-cyclo-hexadienone (BHT-quinol) > 3,5-di-*tert*-butyl-4-hydroxybenzal-dehyde (BHT-CHO). Geometric mean values of total TP concentrations were 555 ng/g and 131 ng/g for urban and rural indoor dust samples, respectively. A preliminary estimated daily intake calculation at dust ingestion scenario suggested additional concerns might be paid to simultaneous exposure of several SPA analogues and TPs besides current focus on BHT exposure risks.

1. Introduction

The environmental occurrence and human exposure of new anthropogenic chemicals have received increasing public scrutiny in recent years, especially for the high production volume (HPV) chemicals with wide commercial applications (Howard and Muir, 2010; Muir and Howard, 2006). Among the various HPV chemicals, an increasing awareness has been raised to the synthetic phenolic antioxidants (SPAs), which are largely used in rubber, plastic, cosmetic formulations, and pharmaceuticals to retard the oxidation process (Demertzis and Franz, 1998; Rodil et al., 2010). SPAs generally present a basic common structure that the phenolic ring is substituted with hindered alkyl groups in *ortho*-positions of the aromatic ring (Brocca et al., 2002). Addition of SPAs is the most commonly used method to retard the oxidation reactions that undergo in all polymeric materials (Rodil et al., 2010).

As additives in polymer matrices, SPAs are likely to leach out by abrasion and volatilization to contaminate the surrounding environment in a manner similar to other additives such as organic phosphate flame retardants and photoinitiators (Liu et al., 2016; Wei et al., 2015). Migrations of certain SPA analogues, i.e. 2,6-di-tert-butyl-4-methylphenol (BHT) and 3-tert-butyl-4-hydroxyanisole (BHA), from packing materials to the contacting water and food simulants (3% actetic acid, 10% ethanol and oil) have been proved in previous studies (Brocca et al., 2002; Gao et al., 2011). BHT was the primary targeted SPA pollutant of concern, which was frequently found in environmental matrixes such as river water, sewage influent and effluent with concentrations varying from part-per-trillion (ppt) to part-per-million (ppm) (Fries and Puttmann, 2004; Liu et al., 2015a; Rodil et al., 2010). A study on the measurement of organic pollutants in indoor environment in Sweden showed that BHT was among contaminates of the highest residue levels in indoor dust, with a mean concentration of 70 μg/g

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(Nilsson et al., 2005). Meanwhile, other SPA analogues, such as 4,4'-butylidenebis (2-(1,1-dimethylethyl)-5-methyl-phenol) (AO 44B25), 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (AO 330) and 2,2'-methylenebis (4-methyl-6-*tert*-butylphenol) (AO 2246), were recently identified in sludge sewage as emerging pollutants (Liu et al., 2015b).

Usage of SPA compounds triggered concerns on the toxic potentials. Long-term exposure of 2,4,6-tri-*tert*-butylphenol (AO 246) was demonstrated to cause liver injury in rats (Matsumoto et al., 1991). Prenatal exposure to AO 44B25 in rats was reported to affect the central nervous system of rat offspring (Takahashi and Oishi, 2006). BHA can modulate and disrupt the endocrine system, and sufficient evidence was found for its carcinogenicity in experimental animals (Grice, 1988; Whysner and Williams, 1996). The effects of BHT consumption on human health are controversial, since some studies indicated a potential link between BHT and cancer, while other studies did not find the relationship (Botterweck et al., 2000; Witschi, 1986).

The quality of indoor environment is crucial to human health as people spend approximately 90% of time indoors (Klepeis et al., 2001). Although mounting evidence showed the importance of indoor dust ingestion as a pathway of human exposure to organic pollutants (Meng et al., 2016; Qi et al., 2014; Wei et al., 2015), there is hitherto little data on indoor concentration levels of SPAs, especially for the analogues with high hydrophobicity and low volatility, which might be easy to absorb on indoor dust and accumulate in human body through dust ingestion. Therefore, the aims of the current study are (a) to report residue levels and composition profiles of novel SPAs and relevant transformation products (TPs) in urban and rural indoor dust; (b) to assess potential risk of human exposure to SPAs via ingestion of indoor dust.

2. Materials and methods

2.1. Materials

Analyte name, structure, abbreviation and other relevant information of the target SPA analytes are shown in the Supporting Information (Table S1). AO 22E46 was supplied by AccuStandard (New Haven, CT). BHT-quinol was purchased from Frontier Scientific Inc. (Logan, UT). Standards of the other analytes were purchased from TCI (Tokyo, Japan). Isotope-labeled standards of 2,6-di-(tert-butyl-d9)-4-methyl (phenol-3,5,O-d3) (BHT-d21) and ^{13}C-tetrabromobisphenol A ($^{13}C_{12}$-TBBPA) were bought from Cambridge Isotope Laboratories (Andover, MA). The purities for all the target analytes were 95% or higher. Silica gel (100–200 mesh size) supplied by Merck (Darmstadt, Germany) was activated at 550 °C for 12 h, and 5% water-deactivated prior to use. Anhydrous sodium sulfate (Na_2SO_4) bought from Sinopharm (Shanghai, China) was baked at 600 °C for 6 h and stored in a sealed desiccator. HPLC-grade hexane (Hex), dichloromethane (DCM) and methanol (MeOH) were obtained from J.T. Baker (Phillipsburg, NJ). Ultrapure water (H_2O, 18.3 MΩ × cm) was generated from Milli-Q purification system (Billerica, MA).

2.2. Sample collection

Individual dust sample was obtained from each of the 75 resident houses in Jinan city (n = 55, the capital of Shandong province, China) and the surrounding rural area (n = 20) in May 2014. According to statistical data from the local government, the per-capita income of urban residents was 2.6 folds higher than rural residents (Statistical bulletin, 2014). The urban houses were equipped with more furniture and electronics than rural houses. Each dust was a mixed sample collected from surfaces in the living room, with an average temperature of 24 °C. Approximately a 0.5 g indoor dust was easily obtained from surfaces of upholstery, furniture, stand fans, and windowsills in each house using wool paint brushes, which covered an area of several square meters. All samples were swept onto aluminum foil, sealed in polyethylene zip bags, and transported back to our lab immediately. Hair in the dust was removed using clean tweezers. Large debris was removed by stainless steel testing sieves to collect dust particles <150 μm in size. To prevent cross-contamination, the wool paint brushes, sieves and tweezers were washed pre- and between sampling intervals by MeOH and ultrapure water, and then air-dried. The dust samples were stored at −20 °C until pretreatment and instrumental analysis.

2.3. Sample preparation and quantitative analysis

The dust samples were extracted by accelerated solvent extraction (ASE), and the dust extracts were cleaned by silica gel packed columns as mentioned elsewhere (Liu et al., 2015a). Briefly, 0.5 g of sample (spiked with 200 ng BHT-d21 and 10 ng ^{13}C-TBBPA) was mixed with 15 g of Na_2SO_4 and extracted by DCM/Hex (3:1, v/v) using an accelerated solvent extractor (ASE 350, Dionex Inc., Sunnyvale, CA). The extraction was conducted at 90 °C and 1500 psi and repeated in three cycles. The dust extracts were concentrated by rotary evaporation to ~2 mL and fractioned on glass columns packed with 8 g of silica gel. Before dust extract loading, the silica gel packed columns were preconditioned by 30 mL of Hex. Then the concentrated extracts were loaded and eluted by 120 mL of DCM/Hex mixture (1:1, v/v). The 120 mL eluates were then concentrated and solvent exchanged into 5 mL of MeOH. Finally, 20 μL of the sample was injected into the instrument for quantification analysis.

The 2695 high performance liquid chromatography coupled with a Quattro Premier XE triple-quadrupole mass spectrometer (HPLC-MS/MS, Waters, Milford, MA) was used for quantification of the target analytes. The mass spectrometer was operated in negative electrospray ionization (ESI) mode. Source and desolvation temperatures were kept at 120 °C and 450 °C, respectively. Desolvation gas flow was 800 L/hr, and cone gas flow was 50 L/hr. The argon pressure in the collision cell was set at 3.8×10^{-3} mbar for MS/MS measurement. Detailed information on the monitored ion transitions and optimized parameters for each analyte is shown in the Supporting Information (Table S2). A SymmetryShield™ 5 μm C18 analytical column (150 × 2.1 mm, Waters, Milford, CT) was selected for the chromatographic separation, with MeOH and H_2O chosen as mobile phases. The column temperature was set at 40 °C, and flow rate for the separation procedure was 0.3 mL/min. The gradient was started at a composition of 25:75 (MeOH/H_2O, v/v). It was first held for 5 min, after which the MeOH was linearly increased to 100% in 10 min and then held for another 10 min. After returning to the initial composition, the column was allowed to re-equilibrate for 3 min.

2.4. Quality assurance/quality control

In order to evaluate the extraction efficiency, 10 dust samples were randomly selected for a fourth extraction. No quantifiable amounts of the target SPAs and TPs were found in the fourth extraction, indicating maximum recoveries of target analytes in the three extraction cycles. Quantification of the analytes was based on external calibration curves, and potential losses during the sample preparation were corrected by the isotopic-labelled standards. As shown in Table S3, concentrations of the single phenolic ring analytes were corrected by BHT-d21, and those of the other SPAs were corrected by $^{13}C_{12}$-TBBPA. Recoveries of the target analytes in matrix-spiked dust samples at 200 ng/g varied from 65% (AO 4426)