Universe Scientific Publishing

DOI:10.18686/ahe.v7i18.9189

Occurrence and Composition Profiles of Several Environmental Endocrine Disruptors in Food Packaging Material from South China

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Abstract: Phthalates, parabens, bisphenols, benzophenones and triclosan (TCS) are ubiquitous in environment, known as environmental endocrine disruptors (EEDs). In this study, those EEDs were analyzed in food packaging materials (n=96) collected from local markets in Guangzhou, South China. Nineteen of 30 target compounds were detected in > 90% samples, and for the first time, TCS (~ 100%) and benzophenones (~50%-100%) were found ubiquitous in food packaging materials. For all samples, concentrations of phthalate were the highest (median: 12100 ng/g), usually thousands of times other EEDs, and were significantly higher in aluminum plastic than those in paper and plastics ($p < 0.01$). The median concentration of TCS was 9.62, 7.51 and 6.31 ng/g in the paper, plastic and aluminum plastic packaging material samples, respectively, but no difference was observed among three categories. No correlation was found between concentrations of phthalates and other EEDs, indicating its special source different from others.

Keywords: Phthalate esters; Parabens; Bisphenol A; Food packing material

Fund Project: Science and Technology Support Plan Project of Langfang Science and Technology Bureau (2022011069) .

Introduction

Environmental endocrine disruptors (EEDs) have drawn considerable attention due to their potential adverse effects to human health (Blumberg 2011). Because of their physical and chemical properties, EEDs are widely used in various industrial and consumer applications.Epidemiological studies have demonstrated that these EEDs can disrupt endocrine system, hormonal balance, and immune system. and researches have indicated the ubiquitous of EEDs in human urine, serum, breast milk, and breast lipid{Zhang, 2013 #158;Asimakopoulos, 2014 #156;Dayan, 2007 #165}, which reflected that human are widely exposure to them.

Diet is an important source, but its contribution to total human exposure doses varied depending on characters of specific contaminants. For instance, previous studies demonstrated that diet was the major source of high molecular phthalates, e.g, diethylhexyl phthalate (DEHP) (Wormuth et al. 2006), and also was the significant source for human exposure to BPA.However, there are limited studies for benzophenone-type UV filters in foodstuffs, though they have already been detected in human urine (Louis et al. 2014).

The ubiquitous of EEDs in foodstuffs indicated the importance to understand where the chemicals come from. One of the potential ways is chemical release from food packaging materials, e.g., phthalates (Bo et al. 2007) and BPA (Lópezcervantes and Paseirolosada 2003b). A study suggested that phthalates exposure levels were significantly decreased by avoiding consumption of food with packaging materials (Rudel et al. 2011), reflecting the migration of phthalates from packaging materials to food. Also, the release of bisphenol analogues from can coating into canned beer was demonstrated by changing stored temperature and time (Xie et al. 2015). In addition, benzophenone added in UV inks was reported to have a pronounced migration potential (Pastorelli et al. 2008).

Considering the importance of diet to EEDs exposure, and limited data of several EEDs in food packaging materials, in the present study, we analyzed several groups of EEDs in 96 food packaging materials samples collected from South China. With these data, we aimed to figure out the contaminant status of these EEDs in food packaging materials in South China and their composition profiles.

Materials and Methods

Analytical standards. Nine phthalates, including DMP, DEP DBP,DIBP, DNHP, BBZP, DEHP, DNHP, DCHP, and DNOP, and their corresponding deuterated (d4) internal standards. Analytical standards of 6 paraben and 9 bisphenol analogues, including MeP, EtP, PrP, BuP, BzP and HepP, BPA, BPAF, BPAP, BPF, BPS, and BPZ, BPG, BPPH and BPBP, as well as TCS, were purchased from AccuStandard (New Haven, CT, USA). Analytical standards of five benzophenone-type UV filter, including BP-1, BP-2, BP-3, BP-8 and 4-HBP, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Isotope labeled $^{13}C_6$-MeP, $^{13}C_6$-BuP, $^{13}C_6$-BPA, $^{13}C_{12}$-BPS and $^{13}C_{12}$-TCS were purchased from Cambridge Isotope Laboratories (Andover, MA), with purity of > 99%. Hexane, methanol, acetonitrile and HPLC grade water were purchased from J.T. Baker (Pillipsburgh, NJ, USA).

Sample collection and preparation. Firstly, the packaging material (~ 0.25 g) was cut into small pieces, spiked with internal standards and put in darkroom overnight. Then, the samples were ultrasonic extraction with 10 mL hexane in Teflon tube for 20 min, with the temperature maintained at 25°C. After shaking by oscillator for 30 min, and centrifugation for 10 min at 4000 rpm, the organic layer was transferred into a clean glass flask. The sample was re-extracted two times. All the extractions were combined and then the final eluate was concentrated to 0.5 mL for instrumental analysis.

Instrumental analysis. Gas chromatography coupled with a mass spectrometer was used for analysis of phthalates in the SIM mode. After the samples injection volume of 1.0 μL with the splitless mode for GC, phthalate targets were separated on a fused-silica capillary column .The injector and ion source temperatures were 280 °C and 250 °C, respectively. The responses of individual deuterated internal standards of the corresponding phthalate esters were used for the quantification. After analysis of phthalates, solvent was changed from hexane to methanol to determine other target EEDs. A Shimadzu Nexera-XZ LC system coupled with an AB-Sciex 5500 triple quadrupole mass spectrometer was used to quantify other target EEDs. Chromatographic separation was achieved using a Betasil C18 column . The injection volume was 5 μL. The MS/MS was selected in multiple reaction monitoring negative ionization modes for target compounds. The mobile phase was 100 % methanol (A) and 10 % methanol in Milli-Q water (B) at a flow rate of 250 mL/min.

Results and Discussion

Detection frequency of EEDs. Our food packaging materials were grouped into 3 categories, including paper (n=22), aluminum plastic (n=47) and plastics (n=27). Among the 96 food packaging samples, at least one individual target compound was found in each sample . 19 of the 30 compounds were frequently detected, with frequencies > 90% in food packaging materials, including DEP, DIBP, DBP, DEHP, BPBP, BPZ, BPG, BPPH, BPAP, BPAF, BPHP, BPS, MeP, EtP, PrP, BP-3, BP-1, BP-8 and TCS, whereas, DCHP, BuP, BzP and HepP were rarely detected, with detection frequencies < 15%. In addition, for the first time, we found the ubiquitous TCS (~ 100%) and benzophenone-type UV filters (~50%-100%) in food packaging materials collected from South China. No differences in detection frequency were found among three material categories. The high detection frequencies of target EEDs demonstrated a widespread of EEDs in those samples, indicating the potential food contamination (Guo and Kannan 2012).

Total concentration of EEDs. For all samples, concentrations of $\sum_9$Phthalate were the highest (median value: 12100 ng/g), followed by $\sum_9$Bisphenol (20.7 ng/g), and no differences were found among TCS (7.45 ng/g), $\sum_6$Paraben (3.99 ng/g) and $\sum_5$Benzophenone (1.51 ng/g) . Concentrations of $\sum_9$Phthalate were usually thousands of times to those of other EEDs. As exposure to phthalates may affect human health (Hee et al. 2016), the amount of phthalates in packaging material should be regulated.

Among three categories, no difference was found in concentrations of $\sum_9$Bisphenol, and $\sum_5$Benzophenone in all packaging materials (Figure 1). Concentrations of $\sum_9$Phthalate in aluminum plastic were significantly higher than those in paper and plastics (p <

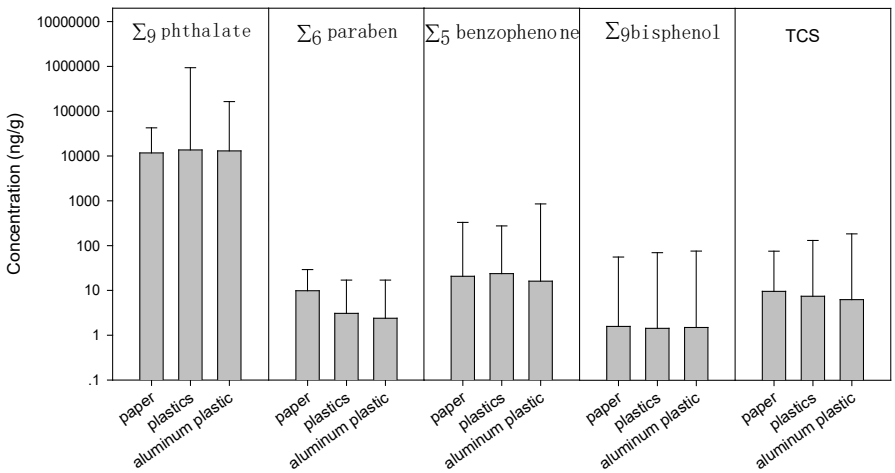

Figure 1. Concentrations of EEDs in different categories of food packaging materials from South China (ng/g)

0.01), and concentrations of $\sum_6$Paraben in paper were significantly higher than those in others ($p < 0.05$). The median concentration of TCS was 9.62, 7.51 and 6.31 ng/g in the paper, plastic and aluminum plastic packaging material samples, respectively, but no difference in concentrations was observed among three categories. The different sequence of EEDs in the three kinds of materials partly reflected their sources, which also reflected by the relationships among those EEDs. No correlation was observed between $\sum_9$Phthalate and any other groups of EEDs in all samples, except for $\sum_5$Benzophenone (Pearson correlation, $p < 0.05$). Further, the relation between $\sum_9$Phthalate and $\sum_5$Benzophenone disappeared if we check correlation based on different categories of packaging material. These results indicated that source of phthalates in samples was different from other EEDs, which partly attributed to the usage of phthalates as additives in plastic materials and the recycle usage of plastics.

In our study, we did not collect glass packaging materials, but plastics, aluminum plastics and paper. Several studies from other countries, such as Belgium (Fierens et al. 2012) and Germany (Gartner et al. 2009), also determined phthalates in various packaging materials. Similar to our study, DEP, DIBP, DBP, BBZP and DEHP were commonly detected in those studies. In addition, the concentrations in samples collected earlier contained relative higher levels, such as samples from Australia in 1996-1997 (the concentration range of DEHP was nd-6630 μg/g) (Balafas et al. 1999). It was not surprised that phthalates were found in plastics and paper packaging materials. As phthalates were used to add into products as plasticizers, although regulations were made to control their amount in food packaging materials, the recycling of old plastics and papers was the possible source.

In conclusion, we analyzed the concentrations of several EEDs in food packaging from South China, and our results suggested that $\Sigma_9$phthalates accounted for > 99% of total target EEDs in all samples. The high amount of phthalates in packaging may be explained by its previous usage as additives added into products and plastic materials recycle. In addition to phthalates, we also found a lot of parabens, bisphenol A and its analogues, benzophenones and TCS in food packaging materials. Our results indicated that the contaminations of EEDs in foodstuffs are partly from their packaging materials.

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