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Short Communication

Flame retardants on the surface of phones and personal computers

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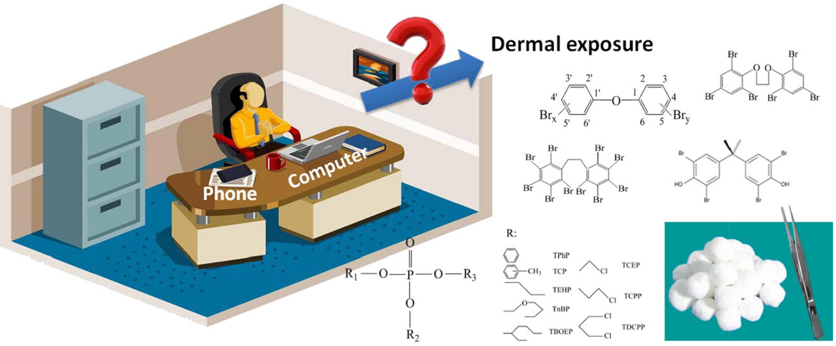
HIGHLIGHTS

- Flame retardants were measured on wipes of phones and PCs.
- TPHP and TCIPP were the most abundant FRs on phone wipes and PC wipes.
- FR levels on phone and PC wipes varied with brands.
- Usage time and time after production were not correlated with levels of most FRs.

GRAPHICAL ABSTRACT



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ABSTRACT

Mobile phones and personal computers (PCs) are essential products that are frequently contacted in daily life. Thus, phones and computers containing flame retardants (FRs) may play vital roles in human exposure to FRs. We measured several FRs, including polybrominated diphenyl ethers (PBDEs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), tetrabromobisphenol (TBBPA), and phosphate flame retardants (PFRs), on the surfaces of phones and PCs (laptop keyboards and mice). Triphenyl phosphate (TPHP, 228 pg/cm^2) and tris(chloroisopropyl) phosphate (TCIPP, 43 pg/cm^2) were the most abundant chemicals on the surfaces of phones, while TPHP (65 pg/cm^2), TCIPP (48 pg/cm^2), and DBDPE (22 pg/cm^2) were dominant on the surfaces of PCs. The usage time and time after the production of the electronics were not significantly correlated with the FR concentrations, except for that of BDE 209. The concentrations of FRs differed on the surfaces of different brands of electronics. Dermal contact with the surface of electronics may contribute to human exposure to FRs, which should be of concern.

1. Introduction

Flame retardants (FRs) are additives widely applied in textiles, foams, plastics, and electronic products. Polybrominated diphenyl ethers (PBDEs) have been used as FRs in commercial products for decades (de Wit, 2002). However, because of their persistence, bioaccumulation, and toxicity in the environment and biota, PBDEs have been phased out worldwide (UNEP, 2009; US EPA, 2009). The occurrence and potential health risks of emerging flame retardants, such as 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and phosphate flame retardants (PFRs), have raised

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concern in recent years with the phase out of PBDEs (Covaci et al., 2011; van der Veen and de Boer, 2012). Previous studies have reported that these emerging FRs were detected ubiquitously in air, dust, soil, sediment, and biota samples (Covaci et al., 2011; van der Veen and de Boer, 2012). Moreover, these FRs are suspected to be toxicants (Meeker et al., 2013; WHO, 1998). For example, a previous study showed that higher levels of tris(1,3-dichloroisopropyl) phosphate (TDCIPP) in house dust may be associated with altered hormone levels and lower semen quality in males (Meeker and Stapleton, 2010). Tri(2-chloroethyl) phosphate (TCEP), TDCIPP, tris(chloroisopropyl) phosphate (TCIPP), and tris(2-butoxyethyl) phosphate (TBOEP) are suspected to be carcinogenic (WHO, 1998). TDCIPP and triphenyl phosphate (TPHP) could disturb the sex steroid hormone balance in human adrenal cell lines (Liu et al., 2012). TDCIPP, TBOEP, and TPHP exhibited in vitro estrogenic and anti-androgenic effect on human osteosarcoma cell lines exposed to indoor dust extracts (Suzuki et al., 2013).

The human intake of FRs can occur through many routes, such as dietary intake, air inhalation, dust ingestion, and dermal absorption (Abdallah et al., 2015, 2016; Cao et al., 2014; Xu et al., 2016). Contact with FR-containing products was also suspected as a potential human exposure pathway, because FRs on the surfaces of electronics and furniture may be absorbed through the skin (Abbasi et al., 2016; Gallen et al., 2014). In electronics containing FRs, it is possible that FRs will be emitted slowly but continuously from the polymer casings and internal components to the surfaces of the electronics and the surrounding environment. BDE 47 and BDE 99 were identified as the main FRs on PC wipes (Abbasi et al., 2016). In the study of Gallen et al. (2014), BDE 209 was the most frequently detected FR on computer surfaces (67% detection frequency, 7.3–680 ng per wipe), followed by tetrabromobisphenol A (TBBPA) (33% detection frequency, 75 ng per wipe) and hexabromocyclododecanes (HBCDs) (33% detection frequency, 6.9 ng per wipe). Gallen et al. (2014) observed positive associations between the amounts of brominated flame retardants (BFRs) detected on the surface wipes and the amounts of BFRs measured in the destructive testing of consumer products. People are in frequent contact with their mobile phones and personal computers (PCs). Thus, it is necessary to know the occurrence of FRs in phones and PCs, which would help us to gain better knowledge about human exposure to FRs. In the present study, we conducted a preliminary survey of several brominated and phosphate FRs on the surfaces of phones and PCs. We aimed to quantify the concentrations of different FRs on the surfaces of phones and PCs and to identify the influences of the FR patterns on the surfaces of phones and PCs.

2. Materials and methods

2.1. Sample collection

A total of 32 healthy adult volunteers (16 females and 16 males) were recruited in June 2015 in Guangzhou, a megacity located in South China. All participants were asked to complete a simple questionnaire concerning their age, gender, and usage time, as well as the time after production and brands of their phones (all smartphones) and PCs (all laptops). Before sampling, sterile cotton balls (diameter: 2 cm) were immersed in isopropyl alcohol for approximately 10 min. The cotton balls were analyzed in additional experiments, and no target compounds were detected. For each participant, the surfaces of their mobile phones and PC keyboards and mice were gently wiped with cotton balls. The cotton balls were manipulated using pre-cleaned tweezers during sampling.

Both sides of the mobile phones were wiped and regarded as phone wipe samples in the current study, and 26 out of the 32 studied phones did not have detachable protecting covers. For phones equipped with a protecting cover, we wiped the outside surfaces of the cover and phone. The upper side of keyboards and computer mice from laptops were wiped and regarded as PC wipe samples in the current study, as people frequently contact the keyboard and mouse when using laptops. Wipes from the mobile phones, keyboards and computer mice were collected from each participant, wrapped in aluminum foil and placed in a hood to facilitate the ventilation of isopropyl alcohol. Then, the wipe samples were stored at −20 °C until analysis. The surface areas of both sides of the mobile phones and the upper side of the PC keyboards and mouse were calculated according to the dimensions of the electronic device:

$$SA_E = \sum(\text{length} \times \text{width})$$

where SA_E represents the surface area of the electronic device (cm^2) and length and width are in units of cm.

2.2. Sample preparation and analysis

After spiking with internal standards (20 ng for BDE 118 and BDE 128, ^{13}C-α-, β-, and γ- HBCDs, and ^{13}C-TBBPA; 50 ng for ^{13}C-BDE 209, 100 ng for TPHP-d_{15} and tri-n-butyl phosphate-d_{27} (TNBP-d_{27})), the cotton balls were extracted by an ultrasonic bath for 30 min with 15 mL acetone/hexane (1/1 v/v), and the extraction was repeated twice. All extracts were combined, blown to near dryness under a gentle nitrogen flow, and then reconstituted in 200 μL isooctane. The samples were stored in a − 20 °C freezer, and the supernatant was transferred for analysis to remove the precipitation. After analysis of the PFRs, all samples were purified with concentrated sulfuric acid, and the organic phase was transferred prior to the analysis of other BFRs and dechlorane plus (DP). The samples were redissolved in 200 μL methanol before analysis of the HBCDs and TBBPA.

The DP and BFRs, except for HBCDs and TBBPA, were measured using a 7890 Agilent (Santa Clara, California, USA) gas chromatograph (GC) coupled with a 5975 mass spectrometer (MS) and a chemical ionization source in selected-ion monitoring mode. A DB-5HT capillary column (15 m × 250 μm × 0.10 μm film thickness; J&W Scientific, CA) was used to separate the PBDEs (BDEs 28, 47, 99, 100, 153, 154, 183, and 209), BTBPE, DBDPE, *syn*-DP, and *anti*-DP. The instrumental conditions were the same as those for the analysis of octa- to deca-BDEs in a previous study (Zheng et al., 2012). The ions m/z 79 and 81 were monitored for PBDEs, except for BDE 209, BTBPE, and DBDPE. The ions m/z 486.7 and 488.7, 653.8 and 655.8, 494.7 and 496.7 were monitored for BDE 209, DP, and ^{13}C-BDE 209, respectively. PFRs (triethyl phosphate (TEP), tri-n-propyl phosphate (TPP), triisopropyl phosphate (TiPP), TNBP, TCEP, TCIPP, TDCIPP, TBOEP, TPHP, 2-ethylhexyl diphenyl phosphate (EHDPP), and tri(2-ethylexyl) phosphate (TEHP)) were quantified using a Shimazu 2010 gas chromatograph coupled with a mass spectrometer with an electron impact ion source. A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent, USA) was used, and the MS was operated in single-ion monitoring mode, with two characteristic ions acquired for each compound. Detailed information about the analytical parameters of PFRs can be found in a previous study (He et al., 2015). The analysis of HBCDs and TBBPA was performed on an Agilent 1200 series liquid chromatograph (LC) equipped with an Agilent 6410 triple quadrupole mass spectrometer with an electrospray interface working in negative ionization mode and fitted with a XDB-C18 column (50 mm × 4.6 mm × 1.8 μm; Agilent). The m/z transitions were 640.7/79 and 542.7/79 for HBCDs and TBBPA, respectively. The instrument parameters were the same those used for HBCD analysis in our previous study (Zheng et al., 2012).

2.3. Quality control

Quality control (QC) was performed by the regular analysis of procedural blanks, spiked blanks, and spiked cotton balls. Spiked mixtures consisted of 20 ng PBDEs (BDEs 28, 47, 99, 100, 153, 154, and 183), BTBPE, DBDPE, HBCDs (α-, β-, and γ-HBCDs), *syn*-DP, and *anti*-DP; 50 ng of BDE 209; and 100 ng of PFRs (TNBP, TCEP, TCIPP, TDCIPP, TBOEP, TPHP, EHDPP, and TEHP). Procedural blanks contained average