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PBDE emission from E-wastes during the pyrolytic process: Emission factor, compositional profile, size distribution, and gas-particle partitioning☆

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ABSTRACT

Polybrominated diphenyl ether (PBDE) pollution in E-waste recycling areas has garnered great concern by scientists, the government and the public. In the current study, two typical kinds of E-wastes (printed wiring boards and plastic casings of household or office appliances) were selected to investigate the emission behaviors of individual PBDEs during the pyrolysis process. Emission factors (EFs), compositional profile, particle size distribution and gas-particle partitioning of PBDEs were explored. The mean EF values of the total PBDEs were determined at 8.1 ± 4.6 μg/g and 10.4 ± 11.3 μg/g for printed wiring boards and plastic casings, respectively. Significantly positive correlations were observed between EFs and original addition contents of PBDEs. BDE209 was the most abundant in the E-waste materials, while lowly brominated and highly brominated components (excluding BDE209) were predominant in the exhaust fumes. The distribution of total PBDEs on different particle sizes was characterized by a concentration of finer particles with an aerodynamic diameter between 0.4 μm and 2.1 μm and followed by less than 0.4 μm. Similarly, the distribution of individual species was dominated by finer particles. Most of the freshly emitted PBDEs (*via* pyrolysis) were liable to exist in the particulate phase with respect to the gaseous phase, particularly for finer particles. In addition, a linear relationship between the partitioning coefficient (K_P) and the subcooled liquid vapor pressure (P_L^0) of the different components indicated non-equilibrium gas-particle partitioning during the pyrolysis process and suggested that absorption by particulate organic carbon, rather than surface adsorption, governed gas-particle partitioning.

1. Introduction

In recent years, recycling of electrical and electronic wastes (E-wastes) in China has attracted serious attention because they are a significant source of polybrominated diphenyl ethers (PBDEs, Chen et al., 2011). Approximately 80% of the annual amount of globally produced E-wastes, mainly printed wiring boards (PWBs), were input to the southeast coastal areas in China for recycling the reusable electronic components and precious metals on PWBs (Luo, 2014a; Ni et al., 2010). Meanwhile, China itself is the second largest manufacturer and yielded over 6 million tons of E-wastes in 2014 (Balde et al., 2015). However, local recycling techniques that have been adopted by numerous small-scale private workshops in these areas are fairly primitive and rough. For example, the collected PWBs are directly heated using a small coal stove or hot air gun in the open air to melt solder and recycle the reusable electronic components, which is usually called board baking (Guo et al., 2015). After the dismantling step, a majority of the circuit boards with removal of electronic components were incinerated to extract the precious metals; meanwhile, amounts of plastic casings of the household or office appliances, together with other municipal solid wastes, were also burned in local furnaces (Li et al., 2008a). Numerous studies have indicated that various harmful pollutants are released under high temperature conditions during the primitive recycling and treatment processes mentioned above (Ren et al., 2014; Ortuño et al., 2015) such as dioxins, particulate matters (PMs) and PBDEs (Duan et al., 2012; Chen et al., 2011) and result in severe pollution around the disposal areas.

As the commonly used flame retardants in PWBs and plastic casings (Tang et al., 2014), PBDEs received wide concern because of

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their persistence, bioaccumulation/bioamplification, various toxicities (*e.g.*, neurodevelopmental, hepatic, reproductive and immune toxicities), and endocrine disruption effects (Naert et al., 2006; Kodavanti et al., 2010; Usenko et al., 2015; Wu et al., 2015). In the form of the physical addition to PWBs and plastic casings, PBDEs are readily emitted into the ambient air during the pyrolysis process and then enter into the soil and water by dry and wet deposition (Xiong et al., 2015; Matsukami et al., 2016), and human beings are further exposed to them *via* dietary ingestion, inhalation and dermal routes (Si et al., 2016; Wang et al., 2016). As a result, PBDE concentrations in multimedia environments around the dismantling areas of E-wastes were significantly greater than those in other areas (Luo et al., 2014a; Tang et al., 2014). It is crucially significant to investigate the emission factors (EFs) and fate behaviors of PBDEs emitted from E-wastes in the process of recycling as one of the uppermost sources, which could provide fundamental information for source apportionment, establishment and updating of the emission inventory and abatement of PBDEs.

PBDEs in the atmospheric environment mainly originate from the manufacturing segment through the use and disposal of products containing PBDEs (Morf et al., 2005; Li et al., 2008b; Björklund et al., 2012). To date, the emission characteristics of PBDEs from E-wastes under thermal stress have only been investigated by very few studies (Guo et al., 2015; Ortuño et al., 2015). However, insight into the emission characteristics of PBDEs freshly emitted in the process of pyrolysis is still scarce, especially the emission factor, the particle size distribution and the gas-particle partitioning of PBDE congeners in the exhaust fumes of E-waste. Emission factors are vital for estimating the emission inventory of specific pollutants on different spatiotemporal scales or based on various industries, *e.g.*, polycyclic aromatic hydrocarbons (PAHs, Shen et al., 2010, 2013, 2011), and for the subsequent and pertinent reduction of the pollutant. The main emission sources in E-waste dismantling areas are relatively fixed, whereas the local distribution is generally dispersed with random emission activity due to the primitive and rough recycling technique. This situation may lead to an extreme lack of data in regard to the emission factor and the inventory of PBDEs at disposal sites of E-wastes. For example, Guo et al. (2015) recently reported EFs of PBDEs in E-wastes during a thermal process, whereas the samples used were limited by type and size. In addition, the experiments were performed in a nitrogen atmosphere, which is quite different from the field conditions. Consequently, it is urgent to launch more studies (under the simulated field conditions) on emission factors and the behavior characteristics of PBDEs freshly emitted from E-wastes in the process of pyrolysis.

In the current study and using a set of specially designed simulation devices, both particulate and gaseous phase samples from the emitted fumes of different E-wastes in the pyrolysis process were collected and then concentrations of thirteen PBDE congeners were determined. The main objectives are addressed as follows: (1) to estimate the EFs of PBDEs from E-wastes in the recycling process (mainly in the form of pyrolysis) based on the carbon mass balance method; (2) to investigate the compositional profiles of individual PBDEs in exhaust fumes; (3) to characterize the size distribution of particulate phase PBDEs; and (4) to explore the gas-particle partitioning behaviors of freshly emitted PBDEs. It should be noted that in the recycling process adopted by most local workshops, two of the aforementioned sequential stages involved high temperature: one is simply called board baking with recycling of the electronic elements, and the other is incineration of the PWBs after the board baking treatment in the furnace to extract precious metals. In many cases, the amount and mode of the addition of a combustion-supporting agent in the latter stage were somewhat subject to randomness by the local employees in practical operation, and thus, the carbon mass balance method was quite difficult to be directly applied to a quantitative estimation on EFs in the incineration process, which may cause a large deviation and uncertainty. Accordingly, in the present study, we tried to explore the emission properties of PBDEs in the board baking stage of the pyrolysis process, and the subsequent incineration stage for extracting valuable metals will be studied in the near future.

2. Materials and methods

2.1. Experimental materials

After a large quantity of E-wastes were transported to the specific southeast coastal areas in China, PWBs were first dismantled to recycle the reusable electronic components and then incinerated to extract precious metals (such as Au and Cu). Meanwhile, many plastic casings of collected household or office appliances, together with the local municipal solid wastes, were combusted in the furnaces. All of these processes could result in massive emissions of PBDEs. Accordingly, PWBs and plastic casings were selected as the experimental materials. Some wasted household or office appliances, including computer monitors, computer hosts, TV sets, laser printers, air conditioners, refrigerators and washing machines were randomly purchased from the recycling center and covered popular brands of appliances in the local market and the corresponding type and specification were recorded. Similar to the disassembling process in the real workshops, PWBs were heated using a hot air gun to melt solder tin and the on-board electrical components were dismantled. For the possible release and loss of PBDEs during this stage, it should be no influence on the EF estimation, because there was no need of collecting the full amount for the carbon mass balance model employed. Then, the remaining boards and plastic casings were chopped into small pieces with a size of 2 cm × 2 cm. A small part of the samples was ground using a grinder (BJ-150, Baojie, China) to measure the elemental carbon content (Elementar Vario MICRO CUBE, Germany) and original PBDEs concentrations and the residual part was employed in the pyrolysis experiments. Detailed information on the materials used is summarized in Table S1 (Supplementary Materials). A total of 41 samples (21 PWBs and 20 plastic casings) were obtained. It should be noted that the PWBs inside the washing machines and refrigerators were excluded, due to their much smaller sizes and much lower contribution to the emission of PBDEs and the fact that both washing machines and refrigerators were mainly recycled for reusable components instead of PWBs.

2.2. Experimental device and sampling

The incorporated experimental device is illustrated in Fig. S1 (Supplementary Materials). A temperature-adjustable electric furnace was selected to carry out the pyrolysis experiments. The size of the furnace chamber was 15 cm × 15 cm × 10 cm. An air inlet was installed at one side of the hearth so that fresh air could freely enter the hearth to ensure aerobic surroundings, which was similar to the situations in the field workshops. The exhaust fumes after pyrolysis were discharged through a leak-proof cylindrical chimney with a diameter of 8 cm and sampled at the chimney outlet. The temperature in the process of board baking and recycling of the plastic casings often fell in the range of 200–300 °C (Guo et al., 2015). To ensure a complete reaction, the temperature of the electric furnace was set at approximately 320 °C, which was slightly higher than the reported range. At the stable temperature, 2 or 3 pieces of PWBs or plastic casings were successively placed into the furnace at an interval of 1 min to guarantee the compositions and flow rate of the exhaust fumes were steady. The concentrations of