BROMINATED FLAME RETARDANTS AND BROMINATED DIOXINS IN THE WORKING ENVIRONMENT AND ENVIRONMENTAL EMISSION – A CASE STUDY AT AN ELECTRONICS RECYCLING PLANT

Takigami H[1], Hirai Y[2], Matsuzawa Y[3], Sakai S[2]

[1] Research Center for Material Cycles and Waste Management, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, 305-8506, Japan

[2] Environmental Preservation Center, Kyoto University, Yoshida Hon-machi, Sakyo-ku, Kyoto, 606-8501, Japan

[3] Ministry of the Environment, 1-2-2 Kasumigaseki Chiyoda-ku, Tokyo, 100-8975, Japan

Introduction

Previous studies show that electronics recycling facilities have higher air concentrations of brominated flame retardants (BFRs) compared to other occupational settings[1, 2], which suggests attention should be paid to occupational exposure to BFRs and their air emission to the environment at the facilities. In this study, we investigated an electronics recycling plant in Japan. At the plant, dismantling and shredding processes of waste television (TV) sets with highest polybrominated diphenyl ether (PBDE) concentrations considered in their housing rear covers were especially focused. Air monitoring for BFRs {i.e., PBDEs, tetrabromobisphenol A (TBBP-A) and hexabromocyclododecane (HBCD)} and polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/DFs) was conducted in the above two processes for TV sets. During investigation, technical countermeasures to reduce particle dust were introduced by the plant and a difference of BFR and PBDD/DF concentrations and patterns in air samples was evaluated before and after taking the measures. Additionally, in order to know sources of occurring BFRs and PBDD/DFs in the air at the dismantling hall, a dust sample collected from the air was compared with TV inside dust and TV housing cover samples in terms with their chemical compositions. Finally, air emission amounts and factors of PBDEs from the two TV recycling processes were calculated by using the obtained data.

Materials and Methods

Description of the facility. At the investigated plant, approximately 600 TV sets were dismantled in a day (approx. 250 operation days/year) to recover valuable metals and dispose of hazardous components properly. The plant had two sections for the treatment of waste TV sets, i.e., a dismantling hall with a storage area (Fig. 1) and a shredder room. TV sets were dismantled manually and separated into several parts of components, i.e., plastic covers (housing cabinets), circuit boards, cables, metals and TV tubes, etc. Suction hood was equipped for spot

ventilation. Additionally, during our investigation, two technical measures were newly carried out to reduce dust at the dismantling site, i.e., (1) a vacuum cleaner was routinely introduced to collect TV inside dust when removing housing rear cabinets, and (2) a portable dust collector was also placed downstream from the removing stage of housing rear cabinets (Fig. 1). Treated gas from the dust collector was discharged into the dismantling hall again. Separated plastic components were shredded to reduce their volume. The flue gas from the shredder was treated by a dust collector before emission to the open air.

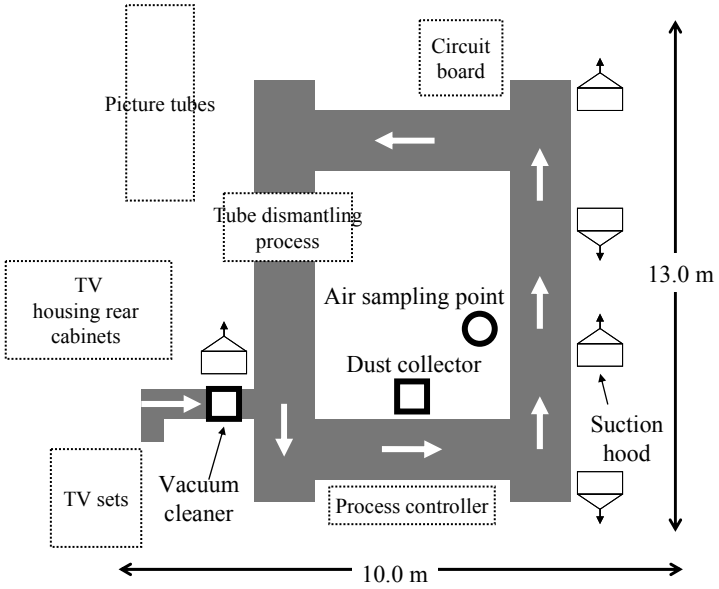

Fig. 1 Schematic diagram of the investigated TV dismantling process. ○, air sampling point; □, newly introduced apparatus for dust collection

Sampling. Sampling was conducted during January to February 2005. Stationary air sampling (140-180 m^3) was conducted by a middle-volume air sampling equipment made from glass fiber filter and polyurethane foam plugs. Flue gas sampling (3.5-4.0 m^3) was performed by a low-volume air sampler following JIS K0311.[3] Dust samples were collected from a dust collector and a vacuum cleaner placed as technical measures in the dismantling hall, corresponding to a stationary air sampling period. The two dust samples were defined as a "dust collected from the air" and a "TV inside dust", respectively. Shredder residues of TV cabinets (composite mixtures) were also sampled.

Analysis. The target substances were extracted in a soxhlet extractor (solids) and by liquid-liquid extraction in a separation funnel (liquids). The crude extracts were cleaned up by using multilayer silica gel column chromatography for PBDE analysis (followed by additional activated carbon chromatography for PBDD/DF analysis). For analyzing TBBP-A, the crude extracts were derivatized (ethylated) and cleaned up by florisil column chromatography, while only florisil column chromatography was needed for HBCD analysis. The final extracts were concentrated and analyzed by HRGC/HRMS.

Results and Discussion

The concentrations of the BFRs and PBDD/DFs in the air of the dismantling hall before and after introducing measures for dust are presented in Fig. 2. PBDEs and PBDD/DFs were identified at 510,000 and 2,400 pg/m^3, respectively, in the air before improvement. DecaBDE dominated the pattern of PBDEs, while OBDF dominated

that of PBDD/DFs. After the technical improvement, each of the sum of PBDEs and PBDD/DFs in the air became one order of magnitude lower. On a congener base, the concentrations of Tetra to DecaBDEs and all the identified PBDD/DF congeners decreased by approximately one or more order of magnitude. In contrast, this decrease was not observed for lower BDEs such as MonoBDEs and DiBDEs and TBBP-A. The "TEQs" for the identified PBDD/DF isomers were calculated on trial by employing WHO-TEFs of their chlorinated counterparts. The calculation also showed a decline of the "TEQs" from 6.7 to 0.93 pg/m^3. The ability of the dust collector was also evaluated by comparing concentrations of BFRs and PBDD/DFs in influent and effluent gas. Removal efficiencies for PBDEs, TBBP-A and HBCD were 84, 97 and 72%, respectively, which supports good performance of the dust collector. Thus, the implemented measures reduced air concentrations of PBDEs and PBDD/DFs effectively as a whole, although it should be noted that the reduced concentrations are still at elevated levels compared to the background. [4]

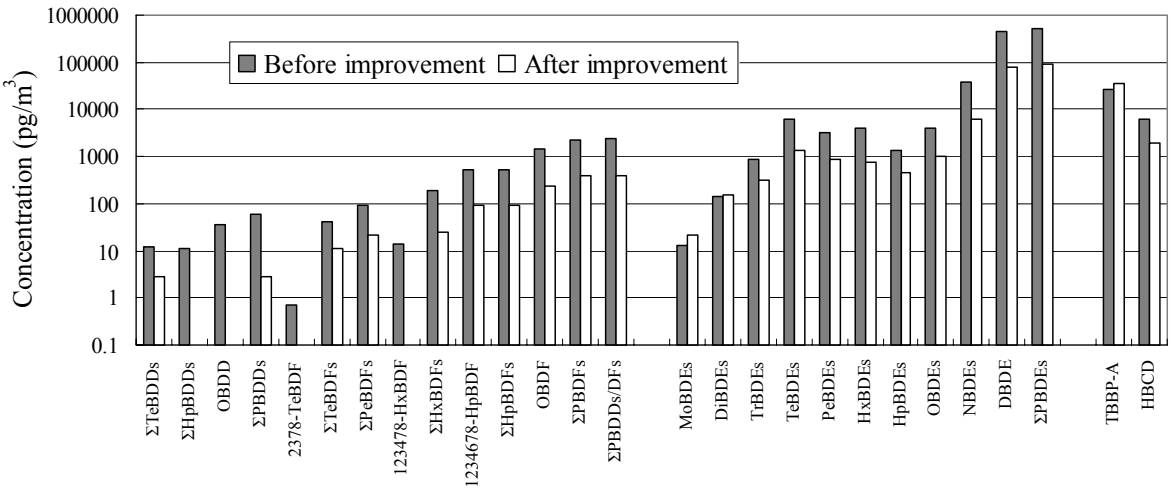

Fig. 2 Air concentrations of PBDD/DFs and BFRs (pg/m^3) before and after introducing technical measures in the TV dismantling process.

The patterns of PBDD/DFs and BFRs present in the dust collected from the air in the TV dismantling hall were compared with those in the TV inside dust, TV housing plastic cabinets and plastic parts of washing machine (as reference) in Fig. 3. The patterns and concentrations of PBDEs in the airborne dust were quite similar to those of the TV inside dust, suggesting the airborne dust derived from the TV inside dust. Namely, the both dust samples were dominated by Tetra and PentaBDE congeners except for Deca and NonaBDEs, differently from the TV cabinets. This finding could point out the importance of removing TV inside dust prior to separating various components to decrease exposure to workers at the plant.

During shredding process of the TV housing cabinets, concentrations of the investigated brominated compounds

were one to two orders of magnitude higher compared to the levels in the dismantling hall air. However, in the treated gas after dust collection, each of PBDD/DFs (sum), PBDEs (sum), TBBP-A and HBCD reduced remarkably by four to five orders of magnitude.

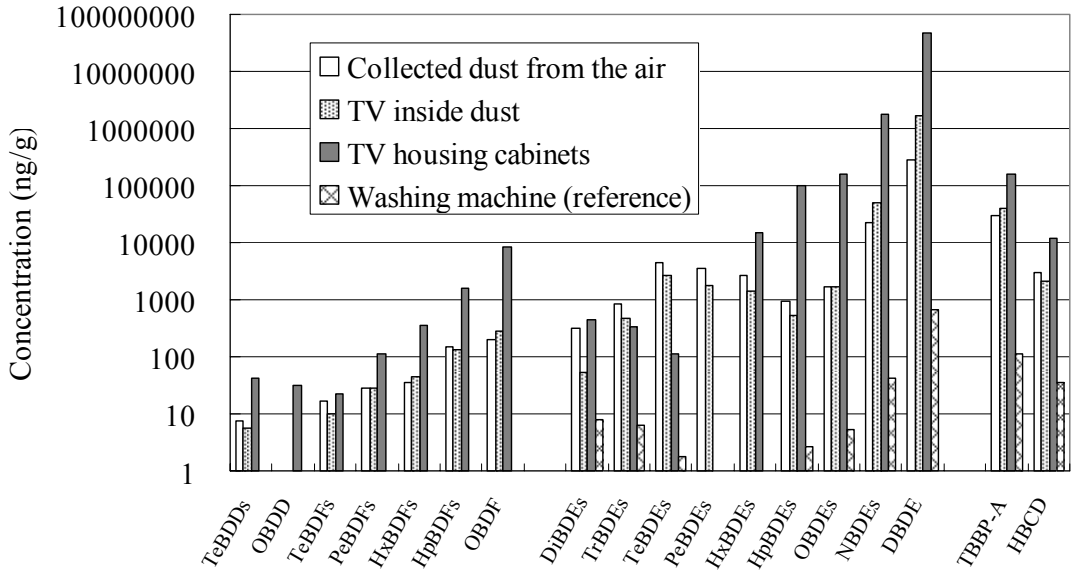

Fig. 3 The differences in concentration (ng/g) in PBDD/DFs and BFRs for two dust samples and two related plastic samples.

Air emission factors and estimated emissions of PBDEs (sum) from the TV dismantling and shredding processes were calculated as shown below.

$$\text{Annual emission (g/y)} = \text{Concentration}_{\text{effluent gas}}\,(\text{g/m}^3) \times \text{Flow rate}_{\text{effluent gas}}\,(\text{m}^3\text{/h}) \times \text{Time}_{\text{operation}}\,(\text{h/y})$$

$$\text{Emission factor (-)} = \text{Annual emission (g/y)} / \text{Annual input to the process (g/y)}$$

Annual emission of PBDEs was estimated to be 0.67 g/y (= 640 ng/m^3 × 1,390 m^3/h × 750 h/y) for the dismantling process (after taking measures) and 0.82 g/y (= 120 ng/m^3 × 3,430 m^3/h × 2,000 h/y) for the shredding process. Air emission factors were further calculated to be 5.9×10^{-8} and 7.3×10^{-8} for the dismantling and shredding processes, respectively, assuming that PBDE input from TV housing cabinet is 45 kg/600 sets/day. The emission potentials of PBDEs were the same magnitude between the two processes at the plant.

References

1. Sjödin A, Carlsson H, Thuresson K, Sjörin S, Bergman Å, Östman C. *Environ Sci Technol* 2001; 35: 448.

2. Thuresson K, Bergman Å, Jakobsson K. *Environ Sci Technol* 2005; 39: 1980.

3. JIS (Japan Industrial Standards) K0311, 2005.

4. Ministry of the Environment of Japan. Survey of PBDD/DF emission in FY 2002, 2003.