BROMINATED DIOXINS EMISSION FROM THE E-WASTE RECYCLING FACILITY IN JAPAN

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Introduction

Brominated dioxins such as polybrominated dibenzo-*p*-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs), and dioxin-like polybrominated biphenyls (dl-PBBs) have been recognized to have similar toxicity profiles to those of their chlorinated analogues[1] and may have contributed significantly in daily human background exposure to the total dioxin toxic equivalents (TEQs) as the results of their unintentional release via the lifecycle of product containing brominated compounds such as brominated flame retardants (BFRs)[2-5]. Therefore, a joint World Health Organization (WHO) and United Nations Environment Programme (UNEP) expert panel recommended to utilize the WHO toxicity equivalency factor (TEF) scheme for the human health risk assessment of brominated dioxin-like compounds[6].

In Japan, the Law Concerning Special Measures against Dioxins of Japan requires the government to promote "the research and study of PBDD/DFs with regard to the extent of their effects on human health, the process of generation, and others". Since 2002, the Ministry of the Environment of Japan (MOE) has conducted a series of field studies to survey the emissions of PBDD/DFs and related compounds from the potential sources related with BFRs[7]. Past surveys clearly revealed that PBDD/DFs tended to be detected in working air and effluents from the facilities recycling the waste of electric household appliances (e-waste) and producing flame-retarded textiles and plastics with BFRs such as deca-BDE and TBPh at concentration in excess of the standards for chlorinated dioxins in Japan (Working air: 2.5 pg WHO-TEQ/m^3, Effluents: 10 pg WHO-TEQ/L).

In this study, brominated dioxins and related compounds in the e-waste recycling facility investigated by MOE were evaluated to reveal the current status of their emission from significant emission source. First, as their sources of human exposure and/or emission into the environment, working environment air and effluent were collected in the e-waste recycling facility. Brominated dioxins and related compounds were measured by using the *in vitro* cell-based reporter gene assay called as the DR-CALUX assay combined with the method separating brominated dioxins from chlorinated dioxins[8]. Samples indicating significant dioxin-like activity were also evaluated by GC-HRMS measurement. And then, the current status and perspective of brominated dioxins and related compounds in Japan were discussed based on obtained results.

Materials and methods

E-waste recycling facility. In Japan, 47 facilities have been established for e-waste recycling (as of July 2018). According to the Law for Recycling of Specified Kinds of Home Appliances (Home Appliance Recycling Law), e-wastes such as TVs, refrigerators, air conditioner and washing machines were collected and recycled properly in the e-waste recycling facilities. It has been reported that the total amount of materials recycled in 47 facilities was 464 kt for e-waste collected in FY2016[9]. Composition ratios of that were 42.4%, 3.6%, 3.3%, 17.0%, 2.7%, and 31.0% for ferrous, copper, aluminum, mixed metal of ferrous and non-ferrous, glass panel for cathode-ray tube (CRT), and plastics. Here, 10 of 47 facilities were investigated for brominated dioxins emission from the e-waste recycling facility in Japan, which were the same facilities as previous MOE investigation. Based on questionnaire survey, the total amount of materials recycled in 10 facilities was 203 kt for e-waste collected in FY2016, which was about 42% of those in 47 facilities.

Sampling. Storage, manual dismantling, shredding and material recovery of e-waste are normally conducted for the shipment of the recycled resources in the e-waste recycling facility. Working environment air in the site of manual dismantling of e-waste such as CRT TV (*n*=8), flat panel display (FPD) TV (*n*=9), refrigerator (*n*=1), air conditioner (*n*=2) and another electric appliance (*n*=1) were collected on a quartz filter and polyurethane foam (PUF) using a high-volume air sampler. The sampling rate and time were approximately 500 L/min and 4 hours in operation, respectively. Final effluents (*n*=12) in operation were collected in amber glass bottles. Wastewaters (*n*=4) before the treatment in the wastewater treatment equipment were also collected. Sampling was conducted during December 2017 to January 2018.

Extraction. For working environment air samples, dioxin-like compounds such as brominated and chlorinated dioxins were extracted from the quartz filter and PUF samples with toluene and acetone, respectively, for 16 hours in a Soxhlet extractor. After filtering the final effluent and wastewater samples, extraction from the glass fiber filter and the filtrate were conducted using toluene for 16 hours in a Soxhlet extractor and a liquid-liquid

extraction with dichloromethane. Obtained extracts were evaporated on a rotary evaporator, the residue was transferred to toluene, and the resulting solution called as crude extract was stored at 4 ºC until analysis.
TCDD-EQ. Separate detection of the chlorinated and brominated dioxins by means of a process involving a silica gel impregnated with 55% sulfuric acid (cleanup column) and a silica gel impregnated with 10% silver nitrate (separation column) with glass columns (Fujifilm Wako Pure Chemical Co. Osaka, Japan) was conducted in this study[8]. Briefly, an aliquot of each crude extract was evaporated and transferred from toluene to *n*-hexane. The *n*-hexane fraction equivalent to 1 m^3 of working environment air or 0.02-0.2 L of water sample was applied to a cleanup column and eluted with *n*-hexane. The eluates were evaporated and loaded onto the separation column. The first fraction, which was eluted with *n*-hexane, contained chlorinated dioxins such as PCDD/Fs and dl-PCBs. The second fraction, which was eluted with 4% (v/v) acetone/*n*-hexane, contained brominated dioxins such as PBDD/Fs. Each fraction was evaporated under a gentle stream of nitrogen, and the residue was re-dissolved in dimethyl sulfoxide for subsequent analytical evaluation. We used the DR-CALUX assay using the rat hepatoma H4IIE cell line[10] obtained from BioDetection Systems B.V. (Amsterdam, The Netherlands) for measurement of the dioxin-like activities of the prepared fractions. The conditions for cell culture and the procedure for the DR-CALUX assay to calculate 2,3,7,8-TCDD equivalent (TCDD-EQ) are described in detail elsewhere[11].
WHO-TEQ. An aliquot of several crude extract with high dioxin-like activity was spiked with ^{13}C-labeled internal standards, the solvent was exchanged from toluene to *n*-hexane, and the resulting solution was cleaned-up by treatment with sulfuric acid, passage through a sulfuric acid- and silver nitrate-impregnated silica gel column, and fractionation on an activated carbon-impregnated silica gel column. Each eluate was evaporated under a gentle stream of nitrogen, and the residue was re-dissolved in nonane containing ^{13}C-labeled standards as syringe spike for subsequent GC-HRMS analysis. We used the GC-HRMS for determination of PBDD/DF, PCDD/DF, and dl-PCB concentrations. The WHO-TEQs for PCDD/DFs and dl-PCBs were calculated by multiplying their measured concentrations by the corresponding WHO-TEFs[12] (WHO-$TEQ_{PCDD/DFs}$). The WHO-TEQs for the PBDD/DFs were also calculated from the WHO-TEFs of their chlorinated analogues (WHO-$TEQ_{PBDD/DFs}$).

Results and discussion
Working environment air. For all working environment air samples (*n*=21), TCDD-EQs for extract containing brominated dioxins (TCDD-$EQ_{PBDD/DFs}$) were 0.32 to 7.5 pg/m^3 (median 1.1 pg/m^3) and TCDD-EQs for extract containing chlorinated dioxins (TCDD-$EQ_{PCDD/DFs}$) were <0.25 to 1.6 pg/m^3 (median <0.25 pg/m^3), indicating that the TCDD-$EQ_{PBDD/DFs}$ tended to be higher than TCDD-$EQ_{PCDD/Fs}$. The TCDD-$EQ_{PBDD/DFs}$ in 3 samples collected in the site of manual dismantling of FPD TV, CRT TV and air conditioner were 3.3, 4.5 and 7.5 pg/m^3, which were higher than the working air standard for chlorinated dioxins in Japan. Because not only PBDD/DFs but also other dioxin-like compounds can be detected by using DR-CALUX assay, PBDD/DFs were analyzed by using GC-HRMS to obtain WHO-TEQ for these samples. As well as TCDD-$EQ_{PBDD/DFs}$, WHO-$TEQ_{PBDD/DFs}$ were 3.7, 6.2 and 6.8 pg/m^3, which were also higher than the standards for chlorinated dioxins in Japan. Based on TCDD-$EQ_{PBDD/DFs}$ and WHO-$TEQ_{PBDD/DFs}$ results, PBDD/DFs concentration of working environment air at FY2017 were equivalent to or lower than those at FY2002 (3.2 to 180 [median 37] pg WHO-$TEQ_{PBDD/Fs}$/m^3, *n*=10) [13)] and FY2011 (0.34 to 9.8 [median 3.1] pg WHO-$TEQ_{PBDD/Fs}$/m^3, *n*=16) [13)]. Removing dust from working environment air was considered effective to reduce potential human exposure and discharge of brominated and chlorinated dioxins in/from the site of manual dismantling of e-waste because more than 85% of TCDD-EQ were detected in dust on a quartz filter, but not PUF (data not shown).
Effluent and wastewater. For all effluent samples (*n*=12), TCDD-$EQ_{PBDD/DFs}$ were <1.0 to 1,500 pg TCDD-EQ/L (median 5.4 pg/L) and TCDD-$EQ_{PCDD/DFs}$ were <1.0 to 50 pg/L (median 1.4 pg/L), indicating that the TCDD-$EQ_{PBDD/Fs}$ of 4 samples and TCDD-$EQ_{PCDD/DFs}$ of 1 sample were higher than the effluent standard for chlorinated dioxins in Japan. Because not only PBDD/DFs but also other dioxin-like compounds can be detected by using DR-CALUX assay, PBDD/DFs were analyzed by using GC-HRMS to obtain WHO-TEQ for these samples. As a result, WHO-$TEQ_{PBDD/DFs}$ (74 pg/L) in 1 sample was higher than the effluent standard for chlorinated dioxins in Japan. Based on TCDD-$EQ_{PBDD/DFs}$ and WHO-$TEQ_{PBDD/DFs}$ results, PBDD/DFs concentration of effluent at FY2017 were equivalent to or lower than those at FY2002 (2.5 to 65 [median 31] pg WHO-$TEQ_{PBDD/Fs}$/L, *n*=6) [13)] and FY2011 (1.4 to 530 [median 88] pg WHO-$TEQ_{PBDD/Fs}$/L, *n*=10) [13)]. For wastewater samples treated in facility (*n*=4), TCDD-$EQ_{PBDD/DFs}$ were 31 to 3,700 pg TCDD-EQ/L and TCDD-$EQ_{PCDD/DFs}$ were 8.5 to 230 pg/L. WHO-$TEQ_{PBDD/DFs}$ in wastewater with high TCDD-$EQ_{PBDD/DFs}$ was 100 pg/L, which was also higher than the effluent standard for chlorinated dioxins in Japan. Removing suspended solid (SS) from water sample was considered effective to reduce potential brominated and chlorinated dioxins emission into the environment from facility because more than 89% of TCDD-EQ were detected in SS on a glass fiber filter, but not filtrate (except 1 effluent sample that 83% of TCDD-$EQ_{PBDD/DFs}$ was detected in the filtrate) (data not shown).

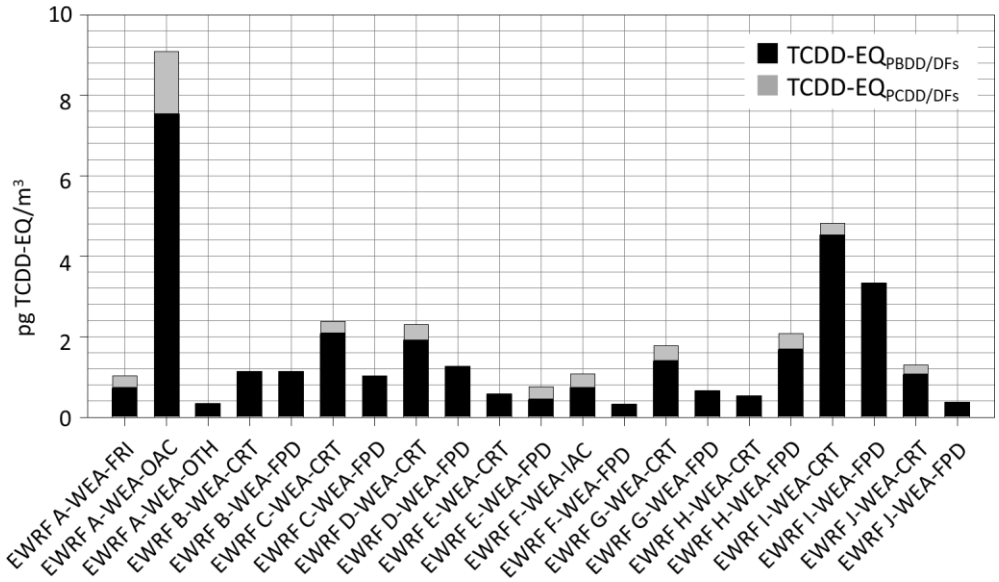

Figure 1 TCDD-EQ in the working environment air from the e-waste recycling facility in Japan
EWRF, e-waste recycling facility; WEA, working environment air; FRI, fridge, OAC, outdoor air conditioner; OTH, other; CRT, cathode ray tube; FPD, flat panel display; IAC, indoor air conditioner

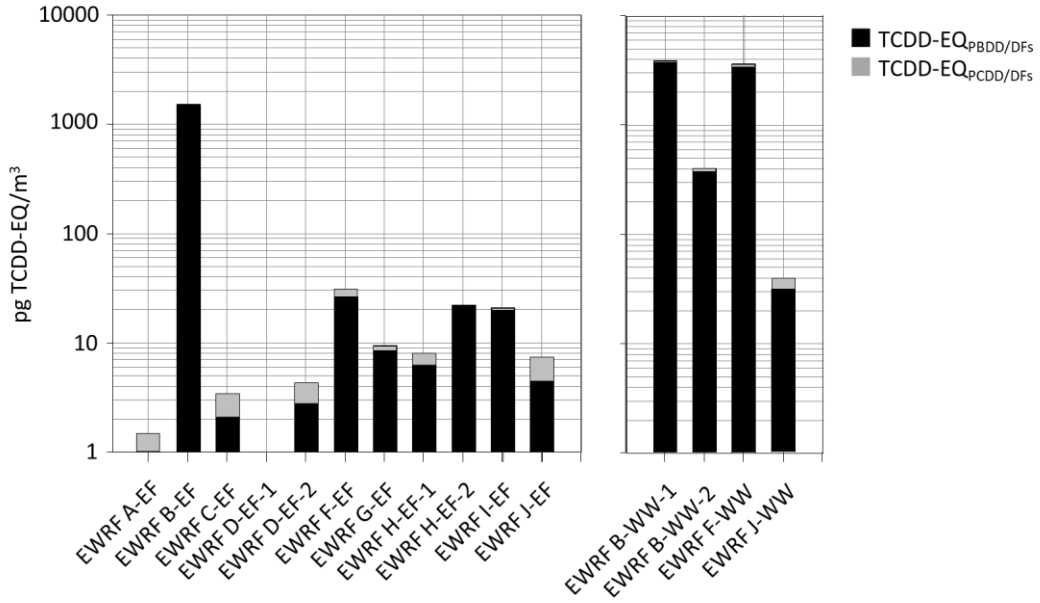

Figure 2 TCDD-EQ in the effluent and wastewater from the e-waste recycling facility in Japan
EWRF, e-waste recycling facility; EF, effluent; WW, wastewater

Conclusion

In this study, by using DR-CALUX assay and GC-HRMS, brominated and chlorinated dioxins concentration were evaluated in working environment air, effluent and wastewater collected from the e-waste recycling facility in Japan, suggesting that PBDD/Fs emission at FY2017 was lower than those at FY2002 and FY2011 and is on a declining trend. Obtained results also indicates that it is important for the environmentally sound management of brominated and chlorinated dioxins to control particulate matter derived from e-waste in the facility. There are other persistent chemicals that indicate response in the DR-CALUX assay but have not yet been detected by GC-HRMS approach.

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